Atomic Scale Processing Focus Topic
Room 317 - Session AP+2D+AS+EM+PS+SS+TF-MoM

Area Selective Processing and Patterning

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

8:20am **AP+2D+AS+EM+PS+SS+TF-MoM-1 Imperfectly Perfect Materials and/or Processes as a Route for ASD***, **Christophe Vallee**,* SUNY POLY, Albany*; M. Bonvalot, M. Jaffal, T. Yeghoyan,* University Grenoble Alpes, LTM, CNRS, France*; N. Posseme, R. Gassilloud, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France **INVITED**

In recent years, many strategies have been presented to selectively deposit a material on a specific surface (area selective deposition), or space direction (topographically selective deposition). Whatever the selective process developed to this end (inherent delay, surface inhibition, surface activation, super-cycles...), it is expected that a perfect material is perfectly deposited on the surface at stake. However, this most often implies that some imperfect material is thereby deposited on surfaces where no growth is expected. Taking this logic a little further ahead, we can even imagine that it may not be at all necessary to develop perfect ALD processes to achieve ALD-based selective deposits.

In this presentation, we will show how imperfect ALD processes can be developed by working out of the ideal precursor ALD window or regime, to adequately lead to ASD processes. We will also show that the requirements of an ideal growth inhibition of no-growth surfaces can be successfully circumvented for ASD processes. Indeed, the simultaneous deposition of a same material on two differing substrates can lead to inherent discrepancies in the materials quality, that can be advantageously taken into consideration in the development of a localized bottom-up growth strategies by adding a selective etching step.

9:00am **AP+2D+AS+EM+PS+SS+TF-MoM-3 Area Selective Deposition on EUV Photoresist***, **Rosanna Robert**,* SUNY College of Nanoscale Science and Engineering*; H. Frost, K. Lutker-Lee,* TEL Technology Center, America, LLC, USA*; C. Vallée,* SUNY College of Nanoscale Science and Engineering

Area selective deposition (ASD) is a key process required for the next generation of nanotechnology. ASD utilizes surface chemistry and reaction modifications to promote growth on one of two different materials. When applying an ASD process to a patterned wafer with both materials exposed, we can selectively grow a film on one surface while blocking growth on the other surface (known as the nongrowth area). One application for ASD is ultra-thin extreme ultraviolet (EUV) photoresist repair to enable continued pitch scaling in the Back End of Line[1]. Pattern transfer fidelity depends on initial line edge roughness (LER) and line width roughness (LWR) values of the EUV resist. Moreover, local critical dimension uniformity (LCDU) for <30 nm critical dimension hole patterning also varies with the initial resist thickness[2]. In this project, we propose to develop an ASD on EUV resists before or alternatively during an etch process to improve LCDU and LER/LWR; in this case, the ASD is used as a corrective step.

To develop an ASD process that is relevant to device manufacturing, we only consider the gases present on a plasma etch chamber as precursors for ASD. We utilize the plasma assistance of the etch chamber to develop an ASD process by Plasma enhanced chemical vapor deposition, rather than by the more commonly exploited atomic layer deposition. This is more challenging since radicals from precursor dissociation are known to be highly reactive on the surface. However, it was recently demonstrated the selective PECVD of a silicon film on SiON surfaces using SiF4/H2 plasma[3].

In this presentation, we will demonstrate ASD by PECVD on SnOx (a EUV resist material) vs SiO-based materials (underlayer) in a 300 mm plasma etch tool, and the impact of plasma precursors and parameters on selectivity. We will show that we can selectively deposit film on SnOx. Results on full wafers and patterned samples will be presented. Thanks to the use of an in-situ plasma diagnostic, such as optical emission spectroscopy, as well as of ex-situ surface diagnostics such as X-ray photoelectron spectroscopy and scanning electron microscopy, we will discuss the mechanisms inherent to the selective growth and discuss the impact of chemistry of neighboring materials and pattern density.

1 J.Church, "Plasma based ASD for EUV resist defectivity reduction and process window Improvement" *AVS* (2021) Nov 2020

2 B. Vincent et al, Proc. *SPIE 11323,* "Extreme Ultraviolet (EUV) Lithography XI,"1132326 (23 Mar 2020)

3 G. Akiki et al, "Origin of area selective plasma enhanced chemical vapor deposition of microcrystalline silicon," *J. Vac. Sci Technol.A* 39 (2021) 013201

9:20am **AP+2D+AS+EM+PS+SS+TF-MoM-4 Impact of Post-Exposure Treatments on TMSDMA-Passivated SiO_2 Surfaces***, **Anthony Valenti**, C. Vallée, C. Ventrice,* SUNY Polytechnic Institute, Albany*; K. Tapily, K. Yu, S. Consiglio, C. Wajda, R. Clark, G. Leusink,* TEL Technology Center, America, LLC

As the scale of semiconductor devices continues to shrink, conventional approaches to fabrication such as photolithographic patterning are becoming limited in their ability to provide the precision and resolution required for smaller and smaller features. Over the last several years, a bottom-up and self-aligned patterning technique known as area-selective deposition (ASD) has been explored. With this technique, the deposition process is manipulated in such a way as to only promote growth on one type of surface on a patterned substrate. This is typically achieved by inhibiting specific surfaces through the selective chemisorption of molecules that are inert to the reactants used for growth of the material of interest. Aminosilane precursors such as *N*-(trimethylsilyl)dimethylamine (TMSDMA) are of recent interest due to their potential use in area-selective atomic layer deposition (AS-ALD). With their strong selective chemisorption on SiO_2 surfaces versus Si and non-oxidized metal surfaces, these precursors can be used to block deposition of metals on SiO_2 while not inhibiting growth on Si or metal surfaces. For aminosilanes to be used as inhibiting precursors in AS-ALD, the resulting layer must maintain its passivation throughout a dozen or more ALD cycles. This study investigates the impact of various common ALD co-reactant/post-exposure treatments on SiO_2 surfaces passivated via exposure to TMSDMA, including ozone exposure, H_2 plasma treatment, and H_2 plasma treatment followed by H_2O vapor exposure. This project also explores using a second inhibitor dosing via NF_3 plasma treatment in order to fluorinate any nucleation sites left vacant on the SiO_2 surface after TMSDMA exposure. These treatments were conducted on samples of TMSDMA adsorbed on Si(100) substrates with 1000 Å thick thermal oxide surfaces. Water contact angle measurements were taken of each sample to determine relative surface passivation of each sample and to monitor temporal degradation of the surfaces over a timescale spanning weeks. Angle-resolved X-ray photoelectron spectroscopy and attenuated total reflection/Fourier transform infrared spectroscopy were performed in order to determine the chemical state of each surface. Temperature programmed desorption measurements were conducted to assess the relative coverage of the inhibiting film on each sample and their stability at higher temperatures.

9:40am **AP+2D+AS+EM+PS+SS+TF-MoM-5 Area-Selective ALD Using Small Molecule Inhibitors of Different Sizes: Single and Sequential Inhibitor Dosing***, **Pengmei Yu**, M. Merkx, I. Tezsevin,* Eindhoven University of Technology, Netherlands*; P. Lemaire, D. Hausmann,* Lam Research Corp.*; T. Sandoval,* Federico Santa María Technical University, Chile*; W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Due to the continuous scaling of semiconductor device features, area-selective atomic layer deposition (ALD) is gaining attention for enabling bottom-up fabrication with atomic-scale control. Area-selective ALD can be achieved by surface deactivation of the non-growth area using inhibitor molecules. Small molecule inhibitors (SMIs) are of great interest due to the vapor-phase application and corresponding industrial compatibility.[1] Our previous work established that SMIs block precursor adsorption by a combination of chemical passivation of surface sites and steric shielding.[2] In this contribution, we compared three SMIs of different sizes for SiO_2 inhibition on the Al_2O_3 surface, namely acetic acid (HAc), acetylacetone (Hacac), and 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd), and explored sequential dosing of two different SMIs to increase the overall inhibitor packing.

We first focused on the use of a single SMI and studied how the size influences their performance. By in-situ spectroscopic ellipsometry and infrared spectroscopy studies, it is observed that using either a smaller (HAc) or a larger (Hthd) SMI than Hacac[3] could improve SiO_2 ALD inhibition. Density functional theory and random sequential adsorption simulations were performed to further understand experimental findings. We found that although both steric shielding and chemical passivation are required for effective precursor blocking by SMIs, neither of them plays a dominating role. As compared to Hacac, HAc performs better due to its small size, yielding denser packing and thereby a higher degree of chemical passivation. Hthd on the other hand, benefits from its bulkiness, resulting in a higher contribution from steric shielding.

In an effort to achieve a higher selectivity, we explored whether sequentially dosing of two different SMIs can lead to higher surface coverage and deactivation. It is found that enhanced precursor blocking of 98.4 ± 0.2 % could be achieved by dosing HAc and Hthd sequentially, which is higher than either 96.0 ± 0.6 % by Hthd or 97.0 ± 0.5 %by HAc solely. Results for various combinations of inhibitors and sequences will be presented.

In summary, this work illustrates that varying the size of SMIs could bring benefits from either higher steric shielding or chemical passivation components for improved precursor blocking performance. In addition, it is demonstrated that combination of SMIs could potentially be an effective strategy for achieving higher selectivity.

[1] A.J.M. Mackus *et al.*, Chem. Mater. 31, 2 (2019).

[2] M.J.M. Merkx *et al.*, J. Phys. Chem. C 126, 4845 (2022).

[3] M.J.M. Merkx *et al.*, J. Vac. Sci. Technol. A 39, 012402 (2021).

10:00am **AP+2D+AS+EM+PS+SS+TF-MoM-6 Role of Catalytic Surface Reactions During Area-Selective Tan ALD for Precursor Blocking Using Aniline Molecules***, **Marc Merkx**[1], I. Tezsevin, P. Yu, R. Heinemans, R. Lengers, E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Federico Santa Maria Technical University, Chile

The semiconductor industry is running into significant issues regarding RC-delays in state-of-the-art interconnect structures. A solution is to selectively deposit the transition metal nitride diffusion barrier on the dielectric via sidewalls but not at the bottom, known as a bottomless barrier structure.[1]. In this contribution, area-selective TaN ALD is investigated using aniline as a small molecule inhibitor (SMI),[2] with the focus on studying the catalytic surface reactions that take place on the metal non-growth area after aniline adsorption.

Area-selective TaN ALD was achieved using a three-step (i.e. ABC-type) ALD cycle using: (A) aniline as SMI, (B) tert-butylimidotris(dimethylamino)tantalum (TBTDMT) as the precursor molecule, and (C) an Ar-H_2 plasma as the co-reactant. This process was found to selectively deposit TaN on dielectric surfaces (e.g. Al_2O_3 and SiO_2) considering the metal surfaces (e.g. Co, Ru) as non-growth area. It was observed that the selectivity of the process is strongly dependent on the employed substrate temperature. At 175 °C only ~1 nm TaN can be deposited selectively, whereas by raising the substrate temperature to 300 °C ~3 nm of selective TaN growth was achieved on Al_2O_3, with respect to Ru as the non-growth area.

An explanation for the strong temperature dependence for the selectivity of this process could be the catalytic reactivity of the metal non-growth area. For example, through density functional theory (DFT) calculations, it was found that aniline can undergo a hydrogenolysis reaction on transition metal surfaces, where the amine group splits off as NH_3 while benzene remains adsorbed on the surface. This reaction eliminates the NH_2 groups from the surface that could otherwise interact with incoming precursor molecules.[3] Experimental and simulation results will be presented to provide insight into the role that catalytic surface reactions play during area-selective ALD on metal surfaces.

[1] Merkx et al., Atomic Limits **7**, (2022) https://www.atomiclimits.com/2022/04/18/

[2] Merkx et al., Chem. Matter **32**, 7788-7795 (2020)

[3] Merkx et al., Chem. Matter. **32**, 3335-3345 (2020).

10:40am **AP+2D+AS+EM+PS+SS+TF-MoM-8 AVS Russell and Sigurd Varian Awardee Talk: Sequential Application of Two Inhibitors to Achieve Area-Selective Atomic Layer Deposition of Dielectric on Metal***, **Tzu-Ling Liu**[2][3], M. Harake, S. Bent,* Stanford University

Area-selective atomic layer deposition (AS-ALD), which provides a bottom-up approach to fabricate patterned structures, has been considered as a prospective solution to overcome the challenges in current semiconductor manufacturing processes. To enable more applications of AS-ALD, it is critical to expand the AS-ALD toolbox to different types of surfaces. Previous studies have successfully demonstrated selective deposition of dielectrics on the dielectric (DoD) regions of metal/dielectric patterns using alkanethiols and phosphonic acids as the inhibitors for metal surfaces. However, doing the reverse pattern transfer, i.e., selective deposition of dielectrics on the metal (DoM) regions, is less well-investigated because selective inhibitor deposition on dielectric over metal is more challenging. Taking organosilane, a common inhibitor choice for dielectric surfaces, as an example, it can also adsorb on metal substrates when native metal oxide is present. Hence, it is important to develop a strategy to protect metal surfaces from the adsorption of organosilane inhibitors for achieving AS-ALD of DoM.

In this work, we demonstrate a two-step strategy to achieve selective deposition of DoM by using two different SAMs with orthogonal surface chemistry, i.e., one SAM preferentially adsorbs on the metal, which serves as a protector to prevent the adsorption of the other SAM onto the metal, and the other primarily adsorbs on the dielectric, which serves as an inhibitor for AS-ALD. We sequentially perform dodecanethiol (DDT) deposition on Cu surfaces, followed by octadecyltrimethoxysilane (OTMS) deposition on SiO_2 surfaces. Since the Cu surfaces are protected by DDT in the first step, OTMS selectively forms a well-packed self-assembled monolayer (SAM) only on SiO_2. With this strategy, we demonstrate AS-ALD of ZnO and Al_2O_3 on Cu (growth surface) over SiO_2 (non-growth surface) after applying a thermal step to selectively remove DDT protector from Cu. The blocking results show that selectivity > 0.9 can be maintained after 35 cycles of ZnO ALD (corresponding to 5.6 nm of ZnO on a reference native SiO_2-covered Si substrate) and 15 cycles of Al_2O_3 ALD (corresponding to 1.4 nm of Al_2O_3), respectively, using this sequential two-step SAM process. Our study helps expand the selective deposition toolbox and provide more possible applications for AS-ALD in next generation electronic devices.

11:00am **AP+2D+AS+EM+PS+SS+TF-MoM-9 Carborane Self-Assembled Monolayers for Area-Selective Deposition***, **Michelle Paquette**, R. Bale, R. Thapa, S. Pinnepalli,* University of Missouri-Kansas City*; J. Bielefeld, S. King,* Intel Corporation

Area-selective deposition (ASD) is an important strategy in improving the fidelity of and/or reducing the complexity of current multi-pattern pitch-division processes. An expanded palette of ASD materials and processes is needed. Boron carbide (BC) has been demonstrated to be a compelling candidate for low-*k* dielectric, etch stop, diffusion barrier, and patterning-assist layers, due to its robust electrical, mechanical, and chemical properties, as well as unique etch chemistry. The molecular carborane precursor is of interest for BC-based self-assembled monolayers (SAMs). This is a symmetric twelve-vertex molecule, with many available and typically sublimable derivatives. For SAM applications, carborane stands out in that its 3D symmetry allows for the formation of well-ordered layers, and the termination of its vertices by labile H atoms allows for cross-linking with a variety of mechanisms including heat, plasma, and radiation (e.g., UV, e-beam). Carborane SAMs can conceivably fulfill various roles in ASD schemes, including as an intrinsically selective functional dielectric layer (e.g., diffusion barrier), sacrificial layer (e.g., hard mask), direct-writeable layer, or blocking layer to facilitate the selective deposition of other materials. We describe progress in the deposition and characterization of carborane SAMs toward the development of a range of ASD schemes and applications.

11:20am **AP+2D+AS+EM+PS+SS+TF-MoM-10 Peter Mark Memorial Award Talk: Reactive Inhibitory Chemistries for Area Selective Depositions and Their Application in Back End of the Line Processes***, **Rudy Wojtecki**[4],* IBM Almaden Research Center **INVITED**

Area selective depositions (ASD) describe self-aligned processes where the chemical contrast of surfaces are exploited to selectively grow a film. ASD can be applied to a variety of fabrication schemes to improve tolerance to overlay errors in fully aligned via schemes or achieve device performance improvements by reduce resistance between interconnect levels in barrier-less contacts that reduce stage delay. While ASD processes are accessible through a variety of methods – differences in surface reactivities between materials, self-assembled monolayers (SAMs) and small molecule inhibitors, to name a few – reactive organic inhibitors and their application in ASD processes will be described. Reactive inhibitor compositions can be selectively deposited on a metal portion of a pre-pattern surface, then undergo (i) a crosslinking reaction or (ii) further chemical transformations used to grow an inhibitory film to a desired thickness. Crosslinking of a monolayer film for ASD was demonstrated with the introduction of diyne moieties into a SAM composition, which is crosslinked under either UV or thermal treatment. These crosslinked monolayers were found to enhance selectivity in an ASD process and reduce defects on patterned substrates.

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[1] **2021 TFD James Harper Awardee**

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

[3] **AVS Russell and Sigurd Varian Awardee**

[4] **Peter Mark Memorial Award Winner**

With synthetic modifications to increase the length of the SAM, further reductions in defectivity was achieved as well as the ASD of TaN. Electron beam irradiation of aliphatic moieties are also known induce crosslinking. With the use of hydroxamic acid head groups the chemical contrast between exposed (crosslinked) and non-exposed regions could be significant enough to enable a patternable ASD process where, as the crosslink density increased the selectivity of the monolayer is further improved. These SAM chemistries require solution-based coating methods but the concept of a crosslinkable inhibitor could also be translated to a vapor phase process, demonstrated with propargyl amine and vinyl pyridine. To tailor inhibitor thickness in strategy (ii) chemically reactive surfaces were exploited where monomers are selectively attached to a metal surface then polymers grown in an area selective manner with tailorable thicknesses, demonstrated with a polynorbornene and poly(vinylpyridine). This tailorable thickness presents several advantages over monolayers – such as enabling ASD on patterns with topography (sharp corners & bends) or the control of lateral overgrowth. These reactive inhibitory chemistries demonstrate an inhibitory chemistry strategy for ASD and their use in back end of the line applications such as fully aligned via, barrier-less contacts or zero-line end extensions.

Biomaterial Interfaces Division
Room 318 - Session BI+AS+PS-MoM

Biomolecular Interfaces and Underwater Adhesion

Moderator: Morgan Alexander, University of Nottingham, UK

8:20am **BI+AS+PS-MoM-1 Supported Lipid Bilayers as Model Systems to Understand Molecular Interactions at Complex Solid/Liquid Interfaces***,* ***Pierluigi Bilotto,*** Centre for Electrochemistry and Surface Technology, Austria*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria

Generating a detailed molecular understanding of complex, simultaneous inter actions at reactive and/or dynamic solid|fluid interfaces is a challenge across disciplines, and has intrigued researchers for decades.[1, 2] Whether it is, for example, in medical adhesives, friction of articular cartilage,[3] or the adhesion of organisms in seawater,[2] complex macroscopic properties at crowded biologic solid|liquid interfaces are mediated by large numbers of individual nanoscale interactions.[4] Exactly this complex competition and molecular structuring at interfaces are central to a multitude of interfacial phenomena, such as membrane transport,[5] membrane conductance, [6,7] cellular adhesion [8] and adhesion regulation in the marine environment. [9]

In our previous works, we characterised a lipid-based model system (LMS) in terms of its stability and bending properties by employing atomic force microscopy and surface forces apparatus. [10] Then, we further modified its outer face with amine-terminating polymers to investigate the specific electrostatic interaction between the amine and a negatively charged mica surface. Then, we examined how interaction forces are affected by the electrolyte concentration, funding a direct exponential like decay between adhesion and electrolyte concentration. Specifically, we found a decrement of 90% in adhesion in a 1M sodium chloride environment. These fundings suggested the presence of a competing mechanism which was confirmed by a kinetic model at the interface involving two competing Langmuir isotherms. Finally, we could estimate ion/surface interaction energies from the experimentally recorded interaction force measurements.[11]

In the talk we will discuss these works and present the new research opportunities coming out from these results.

(1) Israelachvili, J.; Wennerström, H. Nature 1996, 379, 219–225

(2) Stock, P. *et al,* ACS Nano 2017, 11, 2586–2597

(3) Shoaib, T. *et al,* Biomater. Sci. 2020, 8, 3944–3955

(4) Cai, L. *et al,* ACS Nano 2017, 11, PMID: 28383885, 3727–3732

(5) Gage, P. W.; Quastel, D. M. J. The Journal of Physiology 1966, 185, 95–123

(6) Stieve, H.; Bruns *et al* Zeitschrift für Naturforschung C 1978, 33, 574–579

(7) Stieve, H.; Pflaum *et al,* Zeitschrift für Naturforschung C 1985, 40, 278–291

(8) Ohgaki, M. *et al,* Journal of Biomedical Materials Research 2001, 57, 366–373

(9) He, X.; *et al,*Colloids and Surfaces B: Biointerfaces 2016, 146, 289–295

(10) Bilotto, P.; Lengauer, M.; *et al* Langmuir 2019, 35, 15552–15563

(11) Bilotto, P *et al* ACS Physical Chemistry Au 2021, 1, 45-53

8:40am **BI+AS+PS-MoM-2 Recombinant Lubricin Improves Anti-Adhesive, Wear Protection and Lubrication of Collagen II Surface**, *H. Yuan,* Tianjin University, China*;* ***Laura Mears,*** Vienna University of Technology, Austria*; R. Su,* Tianjin University, China*; M. Valtiner,* Vienna University of Technology, Austria

Lubrication in articular joints is regulated by a number of biomolecules including the collagen of the cartilage, lubricin and lipids in the synovial fluid. Camptodactyly-arthropathy-coxa vara-pericarditis syndrome (CACP) is a joint disease, which causes a lack of lubricin, leading to failed lubrication as well as abnormal deposition at cartilage surfaces. Injection of recombinant lubricin (R-LUB) is a promising way to treat the disease. Here, the protein adsorption and lubrication behavior of type II collagen (COL II), mimicking the cartilage surface, upon R-LUB injection were followed by a surface plasmon resonance spectroscopy and surface forces apparatus. The results indicated R-LUB can bind well on COL II surface and the layer of COL II/R-LUB complex exhibited a much lower nonspecific adsorption of BSA (3.25 ng/cm^2) and LYS (0.26 ng/cm^2) compared to those of the COL II layer (32.7 ng/cm^2, 7.26 ng/cm^2), respectively. Normal force measurement demonstrated there were repulsive forces between the COL II/R-LUB complex and different surfaces with -COO$^-$, -NH$_3^+$ and -CH$_3$ groups. Likewise, COL II had a high coefficient of friction ($\mu\sim0.48$) with surface damage at 2 μm/s and wear pressure of 1.56 MPa. In contrast, the coefficient of friction of COL II/R-LUB complex was dramatically decreased to ~0.014-0.13 with surface damage at 13 μm/s, the complex even shows an ultralow coefficient of friction of 0.008 at the lowest loading <3 mN. Furthermore, R-LUB modification boosts the strength of the surface against abrasive wear (damage) of 11.96 MPa, which was 7.7 times higher than that of COL II alone. Hence, R-LUB may act as an anti-adhesive and lubrication layer adsorbed on COL II surfaces to develop strong steric-repulsive interactions and lubrication to prevent direct surface contact. Our results provide fundamental insights into the adsorption and lubrication behavior for understanding biological lubrication, especially using R-LUB for CACP disease treatment.

9:40am **BI+AS+PS-MoM-5 Hyaluronic Acid-Dopamine Conjugate for Facile Deposition onto Collagen I with Enhancing Anti-Adhesion and Lubrication***, H. Yuan,* Tianjin University, China*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria*;* ***Rongxin Su,*** Tianjin University, China

Collagen I matrix (COL I) has been applied clinically for repairing damaged cartilage, but it has poor protein resistance and insufficient lubrication performance, which seriously affects the repairing performance for cartilage. Hyaluronic acid (HA) has good anti-adhesive and lubrication properties, and seems to be a potential candidate to improve treatment with COL I, but it cannot be immobilized onto the collagen surface. Inspired by mussels, dopamine (DA) was chemically grafted to HA to form the HADA conjugate, which could firmly adhere to the surface of COL I by dopamine oxidation and reacted with amine from COL I. The protein resistance and lubrication properties of COL I and HADA-modified COL I (COL I/HADA) surfaces were followed by quartz crystal microbalance with dissipation and surface force apparatus techniques. The optimal modified time of HADA on COL I surface was 8 h. The nonspecific adsorption of bovine serum albumin (BSA) and lysozyme on COL I/HADA were reduced to 1/25 and 1/42 of that on COL I. COL/HADA also displayed very good resistant to high concentrations of BSA. Upon HADA modification, the interaction force between COL I and the surfaces with positive and negative charges sharply decreased from 2-6 mN/m to 0, demonstrating that the COL I/HADA surface had a strong anti-adhesion property. The coefficient of friction of COL I (~0.65) was quite high displaying poor lubricating ability, while that of COL I/HADA reduced to ~0.16. Upon HADA modification, the wear occurred at a shear rate of 14 μm/s, and the surface resistance to abrasive wear (damage) was greatly improved to 9.7 MPa, about 12 times higher than the COL I surface. These results indicated that HADA-modified COL I is a promising anti-adhesive and lubricating joint repair material, especially in the field of osteoarthritis treatment.

10:00am **BI+AS+PS-MoM-6 Anti-Fouling Properties of Amphiphilic Zwitterionic Hydrogels**, ***Lisa Schardt,*** Ruhr University Bochum, Germany*; A. Martínez Guajardo,* University of Potsdam, Germany*; J. Koc,* Ruhr University Bochum, Germany*; J. Clarke, J. Finlay, A. Clare,* Newcastle University, UK*; H. Gardner, G. Swain, K. Hunsucker,* Florida Institute of Technology*; A. Laschewsky,* University of Potsdam, Germany*; A. Rosenhahn,* Ruhr University Bochum, Germany

Hydrogels exhibit excellent biocompatibility and resistance against nonspecific attachment of organisms most likely due to their stable hydration shell.[1] Zwitterionic polymers like the sulfobetaine N-(2-methacryloxy)-ethyl-N,N-dimethylammoniopropansulfonate (SPE) are promising candidates foranti-fouling coatings. However, due to low mechanical strength, their performance in the field is limited.[2] N-butyl methacrylate (BMA) was added in amounts between 0 and 50% to copolymers containing SPE and the photocrosslinker 2-(4-benzoylphenoxy)ethyl methacrylate (BPEMA) to tune the hydrophilicity of the resulting hydrogel properties. The rearrangement of the polymer upon immersion in seawater was characterized by under-water contact angle goniometry. The swelling and resistance against mineral particles were measured with surface plasmon resonance (SPR) and sediment immersion tests. Biological anti-fouling experiments were performed using *Ulva linza* and field tests. Upon immersion in saltwater, the polymer chains rearranged to form hydrophilic surfaces and the degree of swelling depended on the salt concentration. The incorporation of BMA successfully altered the mechanical properties of the coatings resulting in a lower silt uptake. At the same time, the amphiphilicity did not hamper the anti-fouling performance in laboratory assays and a decrease of the settlement was observed in field tests.[3]

[1] A. Laschewsky, *Polymers*, **2014**, 6, 1544-1601.

[2] J. Koc, *Biofouling*, **2019**, 4, 454-462.

[3] L. Schardt, *Macromolecular Rapid Communications*, **2021**, 2100589.

10:40am **BI+AS+PS-MoM-8 Mussel Adhesion: A Fundamental Perspective on Factors Governing Strong Underwater Adhesion***, L. Mears, J. Appenroth, A. Celebi, A. Imre, H. Yuan,* TU Wien, Austria*; P. Bilotto,* CEST Centre for Electrochemistry and Surface Technology, Austria*; R. Su,* Tianjin University, China*; **Markus Valtiner,*** TU Wien, Austria

Tuning interfacial electrochemistry is central to the principle of the strong underwater adhesive of mussels. Here we critically discuss recent progress in the field, and we discuss how interfacial electrochemistry can vary interfacial forces by a concerted tuning of surface charging, hydration forces and tuning of the interfacial ion concentration. Mussel foot proteins contain a number of different functional groups, with much focus directed towards the catechol moiety. Therefore, we discuss some of our recent results in the area of adhesion of different functional groups in a saline environment. We also present new data from electrochemical surface force apparatus experiments that explore the difference in adhesion for oxidized and reduced forms of the catechol functional group against a mineral, mica, in different environments. These results raise interesting questions about the role of the catechol group. We propose new paths into understanding and utilizing redox-proteins and derived polymers for enhancing underwater adhesion in a complex salt environment.

11:00am **BI+AS+PS-MoM-9 Bioinspired Underwater Adhesives Using Amyloids from Commonplace Proteins***, M. Wilson,* NRC Post-doctoral Fellow sited at the Naval Research Laboratory, Chemistry Division*; M. Beasley,* NRC post-doc sited at the Naval Research Laboratory, Chemistry division*; K. Fears,* Naval research laboratory, Chemistry Division*; E. Yates,* US Naval Academy, Chemistry Department*; **Christopher So**[1],* Naval Research Laboratory, Chemistry Division

Barnacles adhere permanently underwater using proteins that are delivered as a liquid, triggered to assemble, and cure as a bulk amyloid material in extreme seawater environments. More cosmopolitan than most other fouling organisms, barnacles rely on these materials to remain stuck at frigid ocean depths, as well as on hot intertidal coasts. We have previously been successful in designing sequences that can mimic the natural glue chemistry and structure, however bridging the gap between natural sequences and materials of practical use remains a challenge. Here, we mimic protein aggregation from the barnacle with unmodified food proteins as model systems and fabricate adhesives by curing them at the adhesive joint. We use temperature and time to control protein assembly and define the relationship between biophysical state and adhesive strength. Using thermal processing, we fabricate adhesives that approach the underwater lap shear strength of commercial marine and contemporary bioinspired chemistries. Though we observe differences in adhesive behavior between the examined proteins and their aggregation state, the presence of amyloids improves underwater performance across all proteins studied. We show that commonplace proteins can be delivered as a liquid, triggered to cure with chemistry or heat, and form strong underwater adhesives at the contact. The aggregation of commonplace proteins is therefore a viable pathway in creating strong underwater adhesives which, like the organisms that use them, can operate in extreme underwater conditions.

11:20am **BI+AS+PS-MoM-10 Incorporation of Antimicrobial Cyclic Peptides in Polymeric Materials***, D. Regan, Q. Lu, D. Barlow, **Kenan Fears,*** US Naval Research Laboratory

Polymeric coatings are used universally to protect structural materials and extend their operational lifetime. Microbial growth on these coatings, if unmitigated, present health risks and can diminish the protective performance of the coatings. For example, fungi have been linked to the degradation of aircraft surface coatings which can lead to corrosion of the underlying metals. After bans on heavy metal mixtures within surface treatments, a commercial void remains for a solution to prevent biodegradation of material surfaces. Building on the advancements within cyclic peptide synthesis, we test the antimicrobial activity of alpha and beta conformations of cyclic peptides against microorganisms of medical and industrial interest. Minimum inhibitory concentration (MIC) and microbial growth assays showed that cyclic peptides exhibited broad spectrum activity against gram-positive and gram-negative bacteria, yeasts, and algae. Furthermore, the cyclic peptides were mixed into a commercial polyester polyurethane coating, Irogran, and exposed to cultured isolates of biodegrading yeasts. For both cyclic peptide-Irogran blends, zero colony forming units were detected after a one-week exposure. These findings demonstrate how synthesized cyclic peptides retain their antimicrobial activity after incorporation into polymeric surface coatings to prevent the growth of problematic microorganisms.

11:40am **BI+AS+PS-MoM-11 Tuning Amphiphilicity of Alginic Acid-Based Polyelectrolyte Multilayers to Enhance Marine Fouling Resistance***, **Jana Karthäuser**, T. Gnanasampanthan, S. Spöllmann, R. Wanka, H. Becker, A. Rosenhahn,* Ruhr University Bochum, Germany

Polysaccharides are among other naturally occurring polymers commonly used in fouling-resistant coatings for both marine and medical applications. The anionic polysaccharide alginic acid (AA) is a non-toxic, eco-friendly, and readily accessible biopolymer that is widely used for biomedical purposes because of its high water-binding capacity. Thus, alginic acid is an interesting and promising building block to produce marine antifouling coatings. Unfortunately, in seawater, the biopolymer loses its antifouling efficacy due to the complexation of bivalent ions. An approach to overcome the susceptibility of charged polysaccharides, such as AA, is the blocking of the carboxylate groups by hydrophobic functional groups. The incorporation of amphiphilic moieties additionally changes the physicochemical properties of the coating and enables the tuning of fouling-resistant properties.[1]Layer-by-layer assembly of polyelectrolytes is a versatile and common technique to produce highly defined and reproducible coatings. The use of different or differently modified polyelectrolytes with opposite charges enables the charge-driven assembly.[2] To introduce amphiphilicity, different degrees of carboxyl groups of alginic acid were modified with pentafluoropropylamine. The influence of the amphiphilicity on the physicochemical characteristics of the modified alginic acid itself as well as of the coatings, when used alternately deposited with polyethyleneimine in multilayers, were investigated. Subsequently, the different degrees of modification of the AA-containing coatings with respect to the non-specific attachment of proteins by surface plasmon resonance spectroscopy and marine fouling organisms by attachment assays were examined in more detail and revealed an improved fouling resistance with increasing amphiphilicity.

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[1] **BID Early Career Researchers Award**

Plasma Science and Technology Division
Room 315 - Session PS-MoM

Plasmas for the Environment and Sustainability: Plasmas-Liquid Interactions, Water, Air, Soil Treatment

Moderators: David Go, University of Notre Dame, **Jeffrey Shearer**, TEL

9:00am **PS-MoM-3 Nitrogen Fixation by Atmospheric Plasma: Effect of Process Parameters on Product Yield and Selectivity***, N. Maira,* Université libre de Bruxelles, Belgium*; A. Remy,* Université libre de Bruxelles, Belgium/ Ghent University, Belgium*; K. Van't Veer,* Université libre de Bruxelles / Antwerpen University, Belgium*; C. Pattyn, N. Roy,* Université libre de Bruxelles, Belgium*; A. Bogaerts,* University of Antwerp, Belgium*; N. De Geyter,* Ghent University, Belgium*; **Francois Reniers**,* Université libre de Bruxelles, Belgium

Nitrogen fixation using atmospheric plasma is a possible alternative route to the Haber-Bosch process. Among these, microplasmas over water, DBD over water and DBD without water can be used to synthesize ammonium, nitrites and nitrates, depending on the reactants used, and the process parameters. The talk will present a summary of results obtained using the 3 types of plasmas mentioned above. Thanks to original setups, the production of nitrogen oxides and ammonia in the gas phase and in the liquid phase will be tracked. It is shown that simultaneous production of nitrates and ammonium can be obtained from pure nitrogen using a microplasma over water (plasma-induced disproportionation). Conditions for nitrite free solutions are established. The effect of the gas composition and the electrodes polarity on the obtained results is shown. The importance of water vapor as a source of OH and H for reactivity is highlighted. For DBDs without water, the influence of the streamers on the NOx synthesis (from N_2 and O_2) and on the NH_3 synthesis (from N_2 and H_2) is evidenced through heat sensitive experiments on one hand, and through modeling on the other hand. It is shown that, for NOx synthesis the streamers temperature have a significant effect on the oxidation mechanism, preventing the ozone route when too hot. For ammonia synthesis, if the streamers are beneficial for nitrogen splitting, it is shown that they also destroy ammonia, which is preferentially formed outside the streamers.

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N.C. Roy et al, Plasma Processes and Polymers, (2021) 18 (3), 2000087

C. Pattyn et al., Green Chemistry, submitted

C. Pattyn et al., Physical Chemistry Chemical Physics (2020) 22 (42), 24801-24812

K. Van't Veer et al. The Journal of Physical Chemistry (2020) C 124 (42), 22871-22883

Acknowledgements : this work is funded by the Belgian Excellence of Science (EoS) "Nitroplasm" project.

9:20am **PS-MoM-4 Fundamental Insights Into Plasma-Liquid Interactions by Combined Experiments and Multiphase Modeling***, **Necip Uner**,* Middle East Technical University, Turkey*; S. Keniley,* LAM Research*; E. Perez, D. Curreli, M. Sankaran,* University of Illinois at Urbana-Champaign

Plasmas in contact with liquids are of interest because of the complex interactions and potential for novel physical and chemical processes. In general, the system is composed of the gas-phase, liquid-phase, and the gas-liquid interface. Experimental measurements have been made in the gas phase and liquid phase of a plasma-liquid process, and more recently modeling has also been performed. There remains a need to compare experiments and modeling to validate simulation outputs and develop predictive capabilities.

This talk will focus on two important aspects plasma-liquid processes: predicting the species densities and heat transfer phenomena near the interface. The focus of our study was a direct-current (DC) operated pin-to-plane electrode geometry with the liquid serving as an electrolyte and a counter electrode immersed in the solution. First, our recent studies on developing a one-dimensional, isothermal but unsteady-state model for coupled plasma-liquid interactions will be presented. Using a drift-diffusion-reaction formalism, plasma and aqueous chemistry was solved for in an argon-salt water system. In this system, one of the reactions that occurs is the formation of hydroxyl radicals, which subsequently produce hydrogen peroxide. We studied potential mechanisms for hydrogen peroxide production with the plasma operated as either the cathode or anode. Experiments were performed in support of modeling to characterize the plasma and measure the aqueous hydrogen peroxide, and both modeling and experimental results show that its production is substantially higher during anodic operation. Most importantly, the model can successfully predict the order of magnitude of H_2O_2 generation rate in the bulk liquid during anodic operation.

In the second part of this talk, it will be shown that a major portion of the energy in the pin-to-plane electrode is dissipated as heat during cathodic operation. Optical emission spectroscopy indicates that even for a discharge power of less than 2 W, the gas temperature may surpass 1000 K in the cathode sheath, which subsequently heats up the electrode. For small electrode geometries, cathode heating is visible due to extensive blackbody radiation, which confirms the gas temperatures measured by spectroscopy. Despite being only 1 mm away from the cathode, infrared thermometry indicates that the water interface remains surprisingly cool, reaching a maximum of only 335 K. These findings suggest that in addition to the inherent local non-equilibrium between the electrons and larger species in the plasma, there exists a very strong thermal non-equilibrium across the plasma as well.

9:40am **PS-MoM-5 Merging the Fundamental and Applied: Understanding Plasma Kinetics and Energetics to Build Better Mousetraps***, **Ellen Fisher**[1],* University of New Mexico **INVITED**

Historically, plasmas have been used extensively to increase the functionality of a myriad of materials for use in a wide range of applications.Despite this storied history, use of plasma-processed materials has been limited by a lack of understanding of fundamental mechanisms.Moreover, the applicability of various processes such as plasma-assisted catalysis is also limited by this lack of knowledge on the basic kinetics and energetics that contribute to plasma-catalyst synergy.This presentation will review a range of systems that have benefited from the use of optical spectroscopy to investigate gas-phase processes in inductively-coupled plasma systems revealing physical and chemical properties of the plasma systems.Perhaps more importantly, these data highlight details of molecule excitation pathways occurring in various plasma systems as well as how various species are involved in gas-surface interactions.Combined with materials characterization studies, these results emphasize the intimate connections between substrates, plasma parameters and fundamental plasma properties, all crucial components to creating better mousetraps.

10:40am **PS-MoM-8 Comparative Investigation of DC Plasma Versus Boron-doped Diamond Electrodes for Electrochemical Degradation of PFOA***, **Jasmine Dinari**,* University of Illinois at Urbana-Champaign*; N. Uner,* Middle East Technical University, Turkey*; P. Baldaguez Medina, M. Sankaran, X. Su,* University of Illinois at Urbana-Champaign

Per- and polyfluoroalkyl substances (PFAS) are a group of persistent man-made chemicals, currently found in water, that stagnate in the environment. There is a need to degrade PFAS such as perfluorooctanoic acid (PFOA) in our water supplies. In the last decade, two methods that have attracted attention for their capability of mineralizing PFAS into fluoride and CO2 are electrochemical processes and plasmas formed at the surface of a liquid.

Here, we performed a comparative investigation of a plasma and one of the most well-studied electrochemical electrodes, boron-doped diamond (BDD), for PFOA degradation. In addition to carrying out the experiments in the exact same direct-current (DC)-powered electrochemical setup, the plasma and BDD were operated as either the anode or the cathode, with the same platinum wire mesh as the counter electrode. While both the BDD and plasma achieved almost complete degradation of PFOA, the optimal configuration for each of them was found to be cathodic for the plasma and anodic for the BDD, with the plasma degrading the PFOA almost 3 times faster. Compared to the BDD, the plasma required more than an order of magnitude higher voltage, but lower current to achieve a similar degradation efficiency. As a result, both the plasma and BDD degradation resulted in similar energy efficiencies.

Fundamentally, the BDD electrode exhibited zero-order kinetics, revealing that PFAS degradation using the conventional electrochemical method was kinetically controlled. On the contrary, analysis using a film model indicated that the plasma degradation kinetics was mass-transfer-controlled because of the extremely rapid reaction kinetics. In addition, we found that in the case of the plasma electrode, the counter electrode played a critical role. Combined with their optimal configurations, these results suggest that an asymmetric device with the plasma as the cathode and the BDD as the anode may lead to enhanced degradation.

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[1] **2020 PSTD Plasma Prize Winner**

11:00am **PS-MoM-9 Integrated circuit Manufacturing with Plasma Activated Chemical Treatment (IMPACT): A Potential Approach for Reducing the Dose-to-Clear in a Commercial Photoresist***, **Christian Williams**, S. Dubowsky, E. Barlaz, S. Marcinko, M. Sankaran,* University of Illinois at Urbana-Champaign*; E. Suga, A. Matsuyama,* TOK America, Japan*; D. Curreli, D. Ruzic,* University of Illinois at Urbana-Champaign

One of the main characteristics that determine how suitable a photoresist formulation is for industrial applications is referred to as the "dose-to-clear", defined as the amount of energy from the light source necessary to remove (in this case positive) resist from the exposed area. This is an important factor when it comes to chemically amplified resists (CARs), as there is a trade-off between line edge roughness and the dose provided. The Illinois Plasma Institute (IPI) along with the Center for Plasma Material Interactions (CPMI) have developed a method[1] where the polymer component of two commercially available photoresists (designed for wavelengths of 193 nm and 13.5 nm) are treated with an atmospheric AC jet plasma with the intent of reducing the bond energies in the polymer. Some Density Functional Theory (DFT) modeling done at the Laboratory for Computational Plasma Physics (LCPP) indicates the injection of a charged species, in this case, solvated electrons can lower the bond energy of polymers such as those commonly used in commercial photoresist formulations. Preliminary experimental results indicate that the treatment leads to the ability of the resist to be removed at lower exposure times (lower dose) for the 13.5 nm resist by up to 20%. There has also been some experimental evidence that there is a reduction in the residue present after the same exposure times between the untreated and plasma-treated samples when using the 193 nm resist. The exposure tool of choice was a 172 nm VUV lamp that is commercially available and was created by Cygnus Photonics. These results were obtained using an optical profilometer to measure the size of the mask patterns and the reductions that take place at varying exposure times. Rheometry (viscosity) measurements have also been done to ensure that the observed effect is not due to reducing the viscosity and therefore the film thickness. Results from a time-dependency study, to determine if the effects are temporary or permanent, will also be discussed in the context of commercial viability and product shelf life, as this will factor into the usefulness of the project in an industrial context. Ongoing efforts towards a pulsed DC plasma jet setup will be discussed as well.

[1] Patent application submitted Nov. 2020

11:20am **PS-MoM-10 Low Power Degradation of Perfluorooctane Sulfonate (PFOS) in Water Using a Nanosecond Pulsed Atmospheric Pressure Plasma***, **Michael Johnson**,* Syntek Technologies*; W. Maza, V. Breslin,* Naval Research Laboratory, Chemistry Division*; D. Boris, T. Petrova, S. Walton,* Naval Research Laboratory

The prevalence and persistence of perfluoroalkyl substances (PFAS) has led to significant concerns over the damage they can have on human health and the environment, particularly when they contaminate bodies of water. Plasma-based water treatments offer a potential solution to this issue, as they offer a rich chemical environment that can degrade contaminants and are flexible enough to operate in different geometries. In particular, atmospheric pressure plasmas driven with short, high voltage pulses produce the requisite chemistry while maintaining high energy efficiency. In this work, a plasma driven with high-voltage (>10 kV) pulses of varying duration (50-400 ns) and frequency (0.5-10 kHz) is investigated for degrading perfluorooctane sulfonate (PFOS) in water. It was found that after exposure to the plasma caused the concentration of PFOS in solution to decrease with repeated passes through the reactor. Increasing the power consumption of the plasma, either by increasing the pulse width or the frequency, improved the rate of PFOS loss but decreased the energy efficiency. For instance, reducing the frequency of the pulse from 10 kHz to 500 Hz decreased the power consumption by over an order of magnitude while requiring about twice as much time to reduce 50% of the PFOS signal. Time-averaged emission spectroscopy showed that increasing the frequency decreased the average electron density of the plasma and while increasing the temperature of the reactor. In contrast, increasing the pulse width from 50 ns to 400 ns did not have a significant impact on the average electron density or the reactor temperature. Infrared (IR) measurements of the reactor indicated that changes in operating conditions caused only modest changes in reactor temperature. Spectroscopy revealed the presence of photons with energies >5 eV were also observed and could contribute to PFOS loss. This work shows that the main factor determining PFOS loss is the contact time between the plasma reactor and the solution, which implies the most energy efficient operating parameters for PFOS degradation comes from minimizing the duration and frequency of the high-voltage pulses to reduce power consumption.

Plasma Science and Technology Division
Room 315 - Session PS+AS-MoA
Plasma Chemistry and Catalysis

Moderators: Michael Gordon, University of California at Santa Barbara, **Floran Peeters**, LeydenJar Technologies, Netherlands

1:40pm **PS+AS-MoA-1 Study of Plasma-Catalyst Surface Interactions for Nitrogen Oxidation***, **Michael Hinshelwood**, Y. Li, G. Oehrlein,* University of Maryland College Park

Cold atmospheric pressure plasma is a promising tool for enhancing thermal catalysis for nitrogen fixation through NO_x formation. Reactive species generated in the plasma are thought to stimulate reactions at the catalyst surface, but the specific interactions are not well understood. We use a plasma-catalysis setup that enables study of such interactions by infrared spectroscopic methods [1]. In this work the formed species of N_2-O_2 interactions in plasma and over a Pt-Al_2O_3 catalyst are analyzed. An N_2/Ar gas stream is flown through an atmospheric pressure plasma jet (APPJ) to the heated catalyst in a confined chamber, and unexcited N_2 or O_2 gas can also be admitted downstream from the plasma source to the catalyst surface. Catalyst surface species are analyzed using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), while gas phase species exiting the catalyst bed are analyzed with Fourier Transform Infrared Spectroscopy (FTIR). Plasma power, catalyst temperature and Ar/N_2 flow are varied to investigate plasma-catalyst interactions. Bare Al_2O_3 is additionally analyzed as a reference material to isolate the effects of the catalyst from the support. Results reveal multiple interactions on the catalyst surface. Downstream gas FTIR shows a slight increase (40%) of total N_xO_y species upon heating the catalyst from 25 °Cto 350 °C suggesting an increase in reactive nitrogen or oxygen species. Additionally, N_2Odecreases upon heating while NO_x densities rise. The catalyst also promotes oxidation of NO to NO_2 compared to the support-only case at 350 °C, a known feature of platinum catalysts.DRIFTS data reveals that the Al_2O_3 support acts to store NO_x species below 450 °C through the formation of surface nitrites and nitrates, necessitating the use of long exposure times. Correlations of downstream FTIR and DRIFTS data will be presented to untangle various interactions and isolate the processes resulting in plasma catalysis. We thank B. Bayer, Dr. A. Bhan and Dr. P. J. Bruggeman for helpful discussions. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under award number DE-SC0020232.

2:00pm **PS+AS-MoA-2 Investigation of the Interaction Between Non-Thermal Plasma Activated Nitrogen and Metal Surfaces***, **Garam Lee**, C. Yan, W. Schneider, D. Go, C. O'Brien,* University of Notre Dame

Non-thermal plasma (NTP)-assisted catalysis has recently gained substantial interest in the heterogeneous catalysis field for enhancing catalytic activity and/or selectivity, as well as for enabling chemical transformations that neither plasma nor catalysis could deliver individually. Despite the promise, the influence of NTP activation of molecules on reactivity at a catalytic surface remains primitive. Here, we report observations of the products and reactivity of plasma-activated nitrogen (N_2) species exposed to polycrystalline Ni, Pd, Cu, Ag, and Au surfaces using a newly-designed multi-modal spectroscopic tool that combines polarization-modulation infrared reflection-absorption spectroscopy (PM-IRAS), mass spectrometry (MS), and optical emission spectroscopy (OES), combined with density functional theory (DFT) models to rationalize those observations. Observations and models indicate that NTP activation provides access to metastable surface nitrogen species that are inaccessible thermally. Those metastable species are characterized using *ex situ* X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), temperature-programmed desorption (TPD), and temperature-programmed reaction (TPR) with hydrogen (H_2) to produce ammonia (NH_3). Models and observations highlight dependence of this reactivity on the identity of the metal surface. Taken together, results shed light on the role of NTP activation on promotion of surface reactivity.

2:20pm **PS+AS-MoA-3 Long-Term Degradation of PTFE in a Low Temperature Oxygen Plasma***, **Tobias Wagner**, T. Zeller, M. Rohnke, J. Janek,* Institute of Physical Chemistry, Justus Liebig University Giessen, Germany

Atomic oxygen (AO) is the most common gas species in the Low-Earth-Orbit (LEO) and responsible for material degradation of the outer shell of satellites and spacecrafts within this space region. As the LEO is also essential for commercial space flights, the degradation process of materials exposed to AO needs to be better understood in order to prevent possibly devastating material failure. Due to its properties, low temperature oxygen plasmas are suited for material degradation studies taking place on earth instead of quite expensive space studies. Here we focus on the long-term degradation of Polytetrafluoroethylene (PTFE), which is often employed on the outside of spacecrafts and therefore exposed to AO. Up to date, there is no complete understanding of the degradation process on the molecular level, which is necessary for materials improvement and new materials development.

For the degradation studies, a self-constructed capacitively driven 13.56 MHz RF reactor was used to generate an oxygen plasma for the simulation of LEO conditions. PTFE was characterised in the pristine state and after AO treatment at different times by ToF-SIMS, XPS, SEM and confocal microscopy. During plasma treatment, the samples show a linear mass loss behaviour. ToF-SIMS surface analysis reveal mass fragments like COF^- or C_3O^+, which shows a clear chemical reaction of oxygen species with PTFE. The presence of these molecular indicators was verified by XPS, where additional carbon and oxygen species were found after treatment. SEM micrographs showed an inhomogeneous degradation on the surface in the first hours similar to actual LEO exposure. For a complete understanding of the degradation progress, mass spectrometric studies of the plasma composition are carried out in situ. Overall, the results show that the reaction of PTFE with AO is occurring on a chemical rather than a physical path, with the fragmentation of long carbon chains into smaller fragments likely driving the material degradation.

2:40pm **PS+AS-MoA-4 Study of Elastomer Degradation in Processing and Cleaning Plasma Chemistries***, **Nicholas Connolly**, D. Barlaz, R. Garza, D. Ruzic, M. Sankaran,* University of Illinois Urbana-Champaign*; N. Kolliopoulos, G. Lunardi,* DuPont Precision Parts & Solutions

Fluoroelastomer (FKM) and perfluoroelastomer (FFKM) materials are used extensively in seals for plasma processing equipment used to manufacture semiconductors. Chamber etching and cleaning processes, particularly those using fluorine chemistry, oxygen chemistry, or a mixture of both, lead to the degradation of the elastomer seals. While most decomposition products are volatile, the recognition of seals as a source of chamber contamination in the form of undesired etch products and particle generation is important for robust semiconductor manufacturing processes. Recent emphasis on coatings and filler materials for elastomer seals makes understanding of decomposition conditions an ongoing effort.

This work investigates the relationship between plasma parameters, including electron temperature, plasma density, and radical densities, and elastomer seal degradation in mixtures of SF_6/O_2/Ar plasmas. Various commercial FKM/FFKM materials will be investigated. Langmuir probe analysis is used to characterize electron temperature and density (predicted T_e of 3 eV and density of 1 x 10^{17} m^{-3}), while in-situ thermocouple-based radical probes are used to measure radical densities of oxygen. Efforts towards the development and implementation of an in-situ fluorine radical probe will also be reported. Characterization of the elastomer surface after plasma exposure will be completed using electron microscopy and optical profilometry, as well as testing of mechanical properties of the seals.

3:00pm **PS+AS-MoA-5 Utilizing Optical Spectroscopy to Explore Mechanisms of Plasma-Assisted Catalysis in Model Exhaust Systems***, **Joshua Blechle**,* Wilkes University

With increasing concerns over the environmental presence of nitrogen oxides, there is growing interest in utilizing plasma-mediated conversion techniques. Nonthermal plasma-assisted catalysis (PAC) in particular has shown great potential for continued improvements in exhaust abatement. Advances, however, have been limited due to a lack of knowledge in regards to the fundamental chemistry of these plasma systems, and the complexity of the plasma-surface interface. The sheer number of potential catalysts and the variability in exhaust gas composition further exacerbate these issues.

In order to investigate these interactions, a number of inductively-coupled plasma systems were generated from model exhaust precursors (notably, N_2 and O_2 mixtures). Internal energies of notable diatomic species are determined via optical emission spectroscopy (OES) to explore the trends in energy partitioning with respect to plasma conditions. Repeated measurements in the presence of precious metal (Ag, Pt, and Pd) and alumina surfaces demonstrate a strong vibrational temperature (T_V) dependence with respect to applied power (25-200 W) but a somewhat limited dependence on substrate identity. In addition, very little change in N_2* and N* densities are observed, whereas there are significant decreases in both NO* and O* densities in the presence of all substrates. A series of composite ($Ag/\gamma\text{-}Al_2O_3$) catalysts with varying Ag loading are also studied, with T_V's ranging from ~2500-5100 K, with the highest temperatures reached for raw alumina systems, demonstrating a Ag-mediated vibrational quenching.

To further explore catalytic behavior, kinetic trends are observed via time-resolved OES, with rate constants determined for both the formation and destruction of relevant excited states. Correlating these data with measured densities and temperatures allows for unique insight into the plasma-surface interface and the mechanisms by which these processes occur. Expanding upon the library of system conditions and increasing the complexity of the exhaust gas model will serve as a foundation for improved design and implementation of PAC methods.

3:20pm **PS+AS-MoA-6 Gasification of Carbon and CO_2 Into CO at Low Vacuum Through Combined Plasma and Heating Exposure***, **Edwin Devid,*** DIFFER, Netherlands*; R. Van de Sanden,* DIFFER & EIRES, Netherlands*; M. Gleeson,* DIFFER, Netherlands

Atmospheric CO_2 concentrations still continue to rise in 2020 [1] and are threatening the goals of the Paris Agreement [2]. By activating CO_2 through plasma, CO_2 is reduced into CO where CO is not only a high-value chemical for the chemical industry but also allow to store renewable electricity into chemical energy via an intermittent way at the cost of CO_2 consumption. Currently, mere CO_2 dissociation through non-thermal inductively coupled Radio Frequency (RF) plasma is not economically viable to obtainboth high CO_2 conversion and energy recovery efficiencies [3,4].

In this experiment, CO_2 dissociation by plasma is assisted by the co-reactant carbon. Through this co-reactant, additional processes will take place that aids the CO_2 dissociation into CO. In low vacuum (~1.3 mbar CO_2), carbon is heated (till 1000 K, in a quartz tray) while being exposed to CO_2 plasma. This process gives increased yields of CO where O_2 gas is consumed by the dominating process: $2C + O_2 \rightarrow 2\,CO$. No evidence of the gas phase back reaction $CO + 1/2O_2 \rightarrow CO_2$ is observed. By usage of isotopic carbon^{13} and modeling of the mass spectrometric data, the different processes operating (i.e. $2C + O_2 \rightarrow 2\,CO$ versus $CO_2 \rightarrow CO + 1/2O_2$ and $CO_2 + C \rightarrow 2\,CO$) are disentangled. Under a buildup ~1.3 mbar CO_2 atmosphere plus combined plasma and heat exposure upon the carbon gives, with increasing temperature a steeply rising of emitted CO at the cost of declining O_2 and CO_2. From the isotopic carbon is determined that after plasma and heat exposure: the surface color, surface area and pore volume has been changed. In addition the sample mass is reduced (carbon consumption up to 36% gravimetrically), confirming that carbon is consumed.

This potentially opens a new way toward O_2 removal during CO_2 dissociation processes by combining plasma with heating of carbon to generate a clean CO_2/CO stream. If the carbon is of a biogenic origin, the process as a whole is sustainable and fossil free CO is generated. Other additional processes that aid to further increase the CO yield (like reverse Boudouard reaction: $CO_2 + C \rightarrow 2\,CO$) help to find ways for industry to reach higher CO yields by both increasing the CO_2 conversion and the consumption of O_2 through the presence of carbon via non-thermal plasma.

[1] IPCC, *Climate Change 2022,* P. R. Shukla et al., Cambridge University Press, Cambridge, NY, USA.

[2] C. Streck et al., Journal for European Environmental & Planning Law, (2016). 13. 3-29.

[3] R. Snoeckx and A. Bogaert, Chem. Soc. Rev., 46, (2017).

[4] Wolf, A. J. et al., The Journal of Physical Chemistry C, 124, 31, (2020), 16806-16819

4:00pm **PS+AS-MoA-8 Investigation of Oxygen Permeation Enhancement with He/O_2 Plasma and SOEC Interaction***, **Xingyu Chen,*** Dutch Institute for Fundamental Energy Research, China*; F. Peeters, F. Smits, W. Bongers, R. van de Sanden,* Dutch Institute for Fundamental Energy Research, Netherlands

High temperature solid-oxide electrolysis cells (SOECs) using oxygen-selective conducting membrane in combination with plasma has shown high conversion efficiencies in nitrogen fixation and CO_2 conversion, which provides a promising method for renewable energy usage and gas conversion. But the underlying kinetics and limiting rates of the plasma-assisted oxygen conducting membrane remain not clear. The plasma-activated species (e.g., by plasma-excitation, dissociation and ionization) may promote the reduction kinetics on the ion-conducting membrane surface. The effects of plasma-induced surface charging and local fields on the exchange kinetics may also play a significant role in the improvement of the oxygen permeation fluxes of the ion-conducting membrane. To understand the interaction of the plasma and the oxygen-conducting membrane, we develop a dedicated plasma-SOEC reactor to investigate the plasma enhanced oxygen permeation mechanism.

In this contribution, we will present the experimental results of the enhancement of the oxygen permeation fluxes owing to the presence of the oxygen radicals and electrons from He/ O_2 low pressure (~1 Torr) plasma. Langmuir probe measurements and optical emission spectrometry and actinometry will determine the plasma properties (electron density, electron temperature and O radical densities etc.) and provide inputs for the plasma-kinetic modelling of the plasma bulk and wall region. The characterizations of the SOEC with different plasma conditions and membrane temperature are conducted to determine the pumping rates (current density) of the oxygen permeation process. Ultimately, the plasma effects on SOEC performance will be quantified, and novel insights into the ion-conducting rate-limiting kinetics will be discussed.

4:20pm **PS+AS-MoA-9 Application of Plasma-Liquid Chemistry to Carbon-Carbon Bond Formation via Pinacol Coupling Reaction***, **Scott Dubowsky**, J. Wang,* University of Illinois at Urbana-Champaign*; N. Üner,* Middle East Technical University, Turkey*; J. Moore, M. Sankaran,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas in contact with liquids have attracted interest for various chemical applications including the degradation of organic pollutants,[1] conversion of abundant feedstocks,[2,3] and more recently, organic chemistry.[4] Compared to other chemical approaches, plasma-liquid chemistry does not require a catalyst material, is electrified, and produces unique reactive species such as solvated electrons, one of the strongest chemical reducing species.[5]

We present an application of plasma-liquid chemistry to the building of carbon-carbon bonds via the well-known Pinacol coupling reaction. In this organic reaction, a carbonyl group is reduced, typically by an electron donating catalyst such as magnesium, to form a ketyl radical anion species. A pair of these ketyl groups then react to form a vicinal diol, which in the presence of a proton donor such as water, leads to the final diol product. Here, we show that the Pinacol coupling reaction is successfully carried out at a plasma-liquid interface without any catalyst. Our study was performed with a direct-current (DC) powered plasma operated in a previously reported electrochemical setup and primarily focused on methyl-4-formylbenzoate (MFB) as the substrate. For an initial concentration of 0.12 M and a constant operating current of 2.3 mA, the yield of the Pinacol product increased with time from 6.1% after 1 h to 34% after 8 h, while the faradaic efficiency correspondingly decreased from 85.7% to 54.2%. Based on nuclear magnetic resonance (NMR) spectroscopy, methyl 4-(dimethoxymethyl)benzoate and 4-(methoxycarbonyl)benzoic acid were also generated as side products. By carrying out scavenger control experiments, we show that the vicinal diol is produced by solvated electron reduction. Finally, we have extended the application of plasma-liquid chemistry to Pinacol coupling of several other aromatic aldehydes and ketones to emphasize its generality.

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4:40pm **PS+AS-MoA-10 Understanding Temperature Inhibition of Methane Conversion in DBD Plasma Using Electrical Characterization and Optical Emission Spectroscopy***, **Ibukunoluwa Akintola**, G. Rivera-Castro, J. Yang, J. Hicks, D. Go,* University of Notre Dame

Non-thermal plasmas (NTPs) produce highly reactive chemical environments made up of electrons, ions, radicals, and vibrationally excited molecules. These reactive species, when combined with catalysts, can help drive thermodynamically unfavorable chemical reactions at low temperatures and atmospheric pressure. We are particularly interested in the direct coupling of light hydrocarbons (e.g. methane) and nitrogen to produce value-added liquid chemicals (e.g. pyrrole and pyridine) in a plasma-assisted catalytic process. In order to effectively create these plasma catalytic systems, it is imperative that there is a fundamental understanding of the plasma-phase chemistry alone. While there have been many studies on nitrogen (N_2) and methane (CH_4) plasmas, there is limited understanding on how changing operating conditions (i.e. feed ratio, plasma power, operating temperature) affect the plasma properties and ensuing plasma chemistry. In this work, we characterize the plasma using electrical measurements and optical emission spectroscopy (OES) and analyze the chemical products using gas chromatography to understand the effects, if any, of varying plasma parameters on product formation. Relevant electrical properties and thermodynamic information such as electron density, vibrational and rotational temperatures, as well as the presence of key plasma species (C-N, C-H, N_2) are compared to relevant products formed during plasma-alone reactions. Results show that different operating conditions lead to changes in energy partitioning in the reaction. Specifically, an increase in temperature leads to a reduction in methane conversion which appears to have an inverse relationship with the vibrational temperatures of C-H species in the plasma.

5:00pm **PS+AS-MoA-11 Optimization of CO_2 Dissociation Efficiency and Conversion in Vortex-Stabilized Microwave Plasmas by Effluent Nozzles***, **Cas van Deursen**,* DIFFER, Netherlands*; H. van Poyer,* DIFFER, Belgium*; Q. Shen,* DIFFER, China*; W. Bongers,* DIFFER, Netherlands*; F. Peeters,* Technical University of Eindhoven, Netherlands*; F. Smits, R. van de Sanden,* DIFFER, Netherlands

Efficiency and conversion in a reverse vortex microwave plasma utilized for CO_2 dissociation are enhanced by considering and optimizing the thermal trajectory of the plasma effluent using a Laval nozzle. The nozzle is used to mix the cold, unconverted gas at the edges of the tube with the hot, dissociated gas in the middle of the flow and to force the gas to accelerate, thereby cooling the effluent. The temperature trajectory of the gas is determined by measuring the gas temperatures of the plasma core and the afterglow using OES and the gas exiting the Laval nozzle using a thermocouple. The effects of the nozzle on the size of the plasma is determined using OES and plasma imaging. The effects of different nozzle diameters on the temperature trajectory and conversion and efficiency are compared to the baseline configuration. Measurements show significant improvements in energy efficiency at close to atmospheric pressures (500 – 900 mbar), especially for higher flows (12 – 18 slm). Results are discussed and explained on the basis of simulations. Options for further improving reactor efficiency and conversion are also discussed.

Atomic Scale Processing Focus Topic
Room 317 - Session AP+AS+EM+HI+PS+SS+TF-TuM

Area Selective Processing and Patterning II

Moderators: Michelle Paquette, University of Missouri-Kansas City, **Christophe Vallee**, SUNY College of Nanoscale Science and Engineering

8:00am **AP+AS+EM+HI+PS+SS+TF-TuM-1 New Precursors and Approaches to ALD and AS-ALD of Metals*, Mikko Ritala,*** University of Helsinki, Finland **INVITED**

Metal ALD is a topic where high technological relevance combines with inspiring and challenging scientific questions. As always, the success of ALD builds on chemistry. There is constant need for new precursors enabling ALD of metals of interest with improved characteristics. A major challenge arise from the strong tendency of metals to agglomerate, hence preventing achieving continuous films at the smallest thicknesses. Lowering of the deposition temperature is of utmost importance to limit the agglomeration. This requires highly volatile and reactive metal precursors and reducing agents. 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine ((Me_3Ge)DHP) is a new reducing that is found more efficient than its earlier reported silicon analogue. $NiCl_2(PEt_3)_2$ in turn represents a series of metal halide adduct compounds of nickel and cobalt where the poorly volatile parent halides are made volatile by proper adduct ligands. The $NiCl_2(PEt_3)_2$ - (Me_3Ge)DHP combination affords deposition of Ni at 110 °C which is the lowest temperature for thermal ALD of Ni so far. (Me_3Ge)DHP enables also deposition of gold. This is the first reductive thermal ALD process of gold.

Area-selective ALD of metals is an important topic for self-aligned thin-film patterning. An entirely new approach to this is area-selective etching of polymers. In these etching processes the selectivity arises from the materials underneath the polymer layers. Both O_2 and H_2 can be used as an etchant gas. Etching gas molecules diffuse through the polymer film, and if they meet a catalytic surface underneath, the molecules become dissociated into their respective atoms which then readily react with the polymer etching it away. On noncatalytic surfaces the polymer film remains. When combined with area-selective ALD, self-aligned etching of polymers opens entirely new possibilities for the fabrication of the most advanced and challenging semiconductor devices. An example is given where the area-selective etching of polyimide from Pt was followed by area-selective ALD of iridium using the patterned polymer as a growth-inhibiting layer on SiO_2, eventually resulting in dual side-by-side self-aligned formation of metal-on-metal and insulator (polymer)-on-insulator.

8:40am **AP+AS+EM+HI+PS+SS+TF-TuM-3 Comparing Interface and Bulk Physicochemical Properties of TiO_2 Deposited by PEALD Assisted by Substrate Biasing on Thermal SiO_2 and TiN Substrates, for Area Selective Deposition Application*, Jennifer Not,*** LTM - MINATEC - CEA/LETI, France*; L. Mazet,* STMicroelectronics, France*; T. Maindron,* Minalogic, France*; R. Gassilloud,* CEA-LETI, France*; M. Bonvalot,* LTM - MINATEC - CEA/LETI, France

To bypass the limitations implied by the miniaturization of electronic components, area selective deposition (ASD) is becoming a key point of focus, as photolithography steps are avoided. This bottom-up promising technique, as opposed to the top down approach inherent to etching, relies on nucleation mechanisms resulting from substrate - precursor interactions. Differing nucleation kinetics may indeed be observed under very same experimental conditions,[1] allowing a growth delay on a surface type while simultaneously promoting growth on a different surface.

Atomic Layer Deposition (ALD) remains a technique of choice to obtain area selective deposition. Based upon the self-limiting nature of surface reactions, this technique enables a conformal deposition with atomic-scale thickness precision, and is gradually becoming a major deposition process in the microelectronic industry.

The ALD reactor used in this study includes an ICP deported plasma source and is equipped with an additional RF polarization kit at the back side of the chuck, enabling plasma ion extraction from the source towards the substrate surface. Depending on the ion incident kinetic energy, which can be tuned as a function of the applied polarization bias, this ion flux can modulate the properties of the thin film under growth, opening new perspectives of physicochemical properties. These properties may also vary according to the substrate surface, making this RF polarization kit an interesting experimental knob for the development for ASD processes[2]. PEALD TiO_2 layers of various thicknesses have been deposited with no air break on a 15 nm-thick TiN layer, as well as on a 100 nm-thick thermal SiO_2 substrate, under various polarization bias power from 0 W to 80 W. The purpose of this work is to physically and chemically characterize the obtained thin films with respect to substrate surface, and to understand how these properties evolve with the film thickness and for various bias values. X-Ray Reflectivity (XRR), Grazing Incident X-Ray Diffraction (GIXRD), *in-situ* and *ex-situ* ellipsometry and Angle Resolved X-ray Photoelectron Spectrometry (AR-XPS) measurements have been performed, providing detailed information on chemical bond formation during nucleation and within the bulk TiO_2 layer, and thin film physical properties, such as thickness, density, roughness and crystallinity. The outcome of this study gives some insight into the benefit of bias for area selective deposition of TiO_2 thin films on TiN against SiO_2.

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9:00am **AP+AS+EM+HI+PS+SS+TF-TuM-4 Area Selective Atomic Layer Deposition of SnO_2 as An Etch Barrier*, Xin Yang,*** University of Texas at Austin*; B. Coffey,* Lam Research Corp*; J. Ekerdt,* University of Texas at Austin

Reactive ion etching (RIE) is widely used in semiconductor nanofabrication processes since it can provide high etch rate, high selectivity, and high anisotropy. Traditional etch masks such as organic photoresists suffer from shortcomings such as low etch selectivity. Other material systems have been investigated to improve the selectivity. $Sn^{(0)}$-containing block copolymers were demonstrated as materials for nanolithographic applications.

Here we propose SnO_2 as a RIE etch mask in fluorine-based etching processes. Tin forms nonvolatile compounds with fluorine enabling tin to function as an etch mask. We establish processes that create SnO_2 grid patterns, which can be transferred into the Si native oxide substrate using SF_6 RIE. The concept is illustrated using a 1000-mesh copper TEM grid as an ultraviolet light shadow mask to generate patterns in polystyrene. SnO_2 patterns are achieved by area selective atomic layer deposition (ALD) using tetrakis(dimethylamino) tin(IV) and H_2O as ALD precursors on a Si native oxide at 170 °C. The selective growth can be directed by the hydrophilicity of the substrate surface. ALD growth of SnO_2 shows no nucleation delay on Si native oxide, which is hydroxylated. By coating the substrate with a polymer such as polystyrene (PS) the reactive sites can be passivated to accomplish selective growth. SnO_2 growth can be blocked up to 50 cycles on H-terminated Si(001), and 200 cycles on cured polystyrene and possibly beyond. Atomic force microscopy (AFM) results show that SnO_2 grown on native oxide has a low roughness of 75 pm, while SnO_2 grown on H-terminated Si has a relative higher roughness of 250 pm indicating a 3-D growth process. To create SnO_2 patterns 20, 50, and 100 ALD cycles of SnO_2 are selectively deposited onto Si native oxide with estimated SnO_2 thicknesses of 1.2 nm, 3 nm and 6 nm, respectively. Samples are then etched with SF_6 RIE for 30 s to 1 min at room temperature and 200 mTorr. AFM results show that SnO_2 grid patterns are transferred into the substrate with a depth of around 300 nm to 1 µm for all three samples. X-ray photoelectron spectroscopy results show that some SnO_2 is transformed into SnF_4 for 100 ALD cycle samples, while all of the SnO_2 is transformed into SnF_4 for 20 and 50 ALD cycle samples.

9:20am **AP+AS+EM+HI+PS+SS+TF-TuM-5 Selective Deposition Two Ways: Chemical Bath Deposition of Metal Sulfides on Organic Substrates***, T. Estrada, **Amy Walker,*** University of Texas at Dallas

Selective deposition has many technological applications. While area selective deposition (ASD) has been widely investigated using atomic layer deposition (ALD), there have been few studies of composition-selective deposition or ASD in which growth occurs at material boundaries. In this talk we shall illustrate these alternate selective deposition methods using two examples.

First, we demonstrate that the composition of tin sulfides is controlled by the bath pH and the interaction of sulfur-containing species with $-CH_3$, -OH and -COOH terminated self-assembled monolayers (SAMs). On -OH terminated SAMs, as the bath pH increases from 10 to 12, the tin sulfide deposited changes from SnS_2 to Sn_2S_3. On -COOH terminated SAMs the deposit is S_2S_3 at pH 10 and SnS at pH 12. In contrast, on $-CH_3$ terminated SAMs the deposit changes from SnS at pH10 to Sn_2S_3 at pH 12. We attribute this behavior to a competition between the repulsion of the chalcogenide ions by the negatively charged carboxylic acid and hydroxyl terminal groups and an increase in chalcogenide ion concentration with increasing bath pH.

Second, we exploit the interaction of the chalcogenide ions with different SAM terminal groups to deposit CuS nanowires at the junction of micropatterned $-OH/-CH_3$ terminated SAMs. We term this method SEmiconductor Nanowire Deposition On Micropatterned substrates (SENDOM). In SENDOM the deposition reaction is kinetically favored on the $-CH_3$ terminated SAMs but transport of reactants is preferred on the hydrophilic -OH terminated SAM. Thus at short deposition times a nanowire forms at the junction of the -OH and $-CH_3$ terminated surfaces.

9:40am **AP+AS+EM+HI+PS+SS+TF-TuM-6 Anatase Crystalline Phase Discovery on Ultra-Thin Layer TiO2Films During Low-Temperature Ald on Fluorine-Rich Carbon Substrates***, **Brian Butkus**, S. Dabas, C. Feit, J. Ganesan, Z. Parsons, X. Feng, P. Banerjee,* University of Central Florida

A novel approach to crystalline anatase phase in atomic layer deposition (ALD) of $TiO_2$by deposited on a fluorine-rich carbon substrate using titanium (IV) isopropoxide (TTIP) and O_2 plasma. In films deposited at temperatures as low as 100 °C and with a thickness of only 4 nm, highly crystalline anatase phases have been observed. Furthermore, when deposited on glass or silicon substrates other than carbon, TiO_2 films consistently produce amorphous films under these conditions. This talk will highlight the unique substrate-driven crystallization of ALD TiO2 and lays the ground rules for selective crystallization using surfaces with suitable initiation chemistries.

An ALD process using a Veeco® Fiji Gen2 ALD system was used to deposit TiO_2 on hydrophobic, polytetrafluoroethylene-coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store). Temperatures of the ALD ranged from 100 °C to 200 °C, and O_2 plasma (300 watts) and water were used as oxidants. Target film thickness ranged from 4 nm to 22 nm. To characterize the films, Raman, Fourier transform infrared spectroscopy (FTIR), and x-ray photoelectron spectroscopy (XPS) were used. AvCarb GDS2230 substrates with an O_2 plasma as an oxidant resulted in anatase TiO_2 films irrespective of thickness, even when deposited at temperatures below 100 °C. However, the anatase phase is significantly weaker when H_2O is used as the oxidant. An interfacial layer of ALD Al_2O_3 suppresses the growth of the anatase phase. Data from XPS indicates that Ti-F bonds form at the pre-deposition stages of films with anatase TiO_2. On non-fluorinated substrates, where the Ti-F bond does not exist, this structurally distinguishes amorphous TiO_2. This fluorine on the surface of the carbon paper serves as a directing agent[1-5] for the application of TTIP to PTFE in a flourolysis reaction, which drives the TiO_2 to crystallize into anatase films.

Fluorine doped crystallization in Ti-O systems has been reported in sol-gel and hydrothermal approaches to synthesize TiO_2 powders.[6, 7]Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase TiO_2 films. With this strategy, surface initiation chemistries can be used to achieve area-selective and in situcrystallization of films.

11:00am **AP+AS+EM+HI+PS+SS+TF-TuM-10 Site-selective Atomic Layer Deposition: Targeting Electronic Defects***, **Alex Martinson**,* Argonne National Laboratory **INVITED**

While ALD is most commonly employed in uniform conformal growth, more selective precursors and processes may allow for more precise synthetic strategies including targeted reaction at subtly unique surface sites including those that lead to electronic defects. We apply a selective hydration strategy to target reaction at the step edges and/or oxygen vacancies of rutile TiO2 and In_2O_3. We computationally and experimentally investigate the feasibility of facet- and site-selective ALD through accurate asymmetric slab models from which the free energy of adsorption at unique surface sites is leveraged to predict step selectivity. Computational evaluation of ALD precursor adsorption free energies on multiple dehydrated facets further refine the feasibility of a temperature-dependent selective hydration strategy. Initial experiments of Al2O3 and Ga_2O_3ALD nucleation on TiO_2single crystals and MgO ALD on In_2O_3broadly support the computational predictions and strategy. The strategies outlined here provide one possible route to selectively target growth at structural defects of oxide surface that may also act as surface or interface electronic defects.

11:40am **AP+AS+EM+HI+PS+SS+TF-TuM-12 Low Temperature Area-selective ALD and ALE of Pd***, H. Nallan, X. Yang, B. Coffey, **John Ekerdt**,* University of Texas at Austin **INVITED**

Thin film deposition and etching approaches may be constrained by the temperature limits for flexible substrates in roll-to-roll processes.We describe a low temperature ALD route to Pd metal film growth at 100 °C that uses $Pd(hfac)_2$ and H_2.The Pd ALD reaction proceeds in the presence of atomic hydrogen; Pd growth nucleates without delay on a Ni metal seed layer that catalyzes H_2 dissociation.Once nucleated, the evolving Pd surface catalyzes H_2 dissociation.To generate the Ni seed layer, a NiO film is first deposited and reduced with an atomic hydrogen source. The 100 °C ALD of NiO using bis(N,N'-di-*tert*-butylacetamidinato)nickel(II) and H_2O as coreactants is highly selective on exposed oxide surfaces and blocked on organic surfaces.NiO films as thin as 0.5 nm, once reduced to Ni^0, effectively seed Pd growth through catalytic area activation.NiO reduction employs an e-beam heated tungsten capillary at 2.5×10^{-6} Torr H_2 that generates atomic hydrogen to reduce NiO films at 100 °C.

In the event non-selective nucleation occurs on passivated regions, we describe a low temperature ALE route to etch clusters/islands on the passivated regions faster than the desired film.This low temperature route exploits the general findings that metal oxides can be etched by a variety of vapor phase etchants, such as formic acid – the issue is controlled oxidation while minimizing damage to adjacent surfaces.We present a low temperature route that involves VUV ($115 \text{ nm} < \lambda < 180 \text{ nm}$) activation of O_2 to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd at 100 °C.Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.Density functional theory is used to study the adsorption of oxidants (O and O_3) and describe O diffusion into the films to understand the kinetic limitations of the oxidation step.

Plasma Science and Technology Division
Room 305 - Session PS1+NS-TuM

Advanced Plasma Patterning: EUV-Based, Multipatterning and Alternative Patterning Approaches (Imprint, DSA, Etc.)

Moderators: Yohei Ishii, Hitachi High Technologies America Inc., **Angelique Raley**, TEL US

8:00am **PS1+NS-TuM-1 EUV Patterning: Plasma Processing Innovations for Single Exposure and Multi-Patterning***, **Katie Lutker-Lee**,* TEL Technology Center, America, LLC **INVITED**

As extreme ultraviolet (EUV) lithography progresses to a mature high volume manufacturing technology, innovations are still required to meet the device scaling and performance requirements. While many of these innovations may take the shape of integration changes, plasma processing will still play an important role in shaping the next generation of technology. In order to advance plasma processing for the next nodes, we must start looking at plasma process development beyond the standard process tuning knobs. New chemistries and techniques must be thoroughly investigated and out of the box thinking must be applied. The applications to which plasma processing can benefit single exposure and multi-patterning techniques are vast, ranging from roughness and profile improvements to the enablement of new integrations techniques.

In this presentation, we will discuss a few of the many innovations we have investigated to overcome the challenges of EUV patterning. It is well known that EUV lithography suffers from stochastically driven defectivity, in particular, feature breaks and bridges, and high roughness.[1] Plasma based process improvements, including etch process co-optimization with films, and selective deposition, have provided critical improvements in this area.[2,3] Processes such as selective deposition also open the door for innovative integration schemes that would otherwise be inhibited.[4] The advent of high-NA EUV lithography will present its own unique challenges, including new materials, in particular metal containing resists, and even smaller feature sizes, in addition to the known challenges of the current generation of EUV lithography.[5] Advanced plasma processing, especially etch, will play an important role in overcoming these hurdles.

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8:40am **PS1+NS-TuM-3 Reduction of EUV Resist Damage by using Neutral Beam Etching***, N. Soo,* School of Advanced Materials Science and Engineering, Sungkyunkwan University, Republic of Korea*;* ***Geun Young Yeom,*** School of Advanced Materials Science and Engineering, Sungkyunkwan University / SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, Republic of Korea

Even though Extreme Ultra Violet (EUV) lithography has the advantage of implenting a finer pattern compared to ArF immersion lithography due to the use of 13.5 nm instead of 193 nm as the wavelengh of the light source, due to the low energy of EUV light source, EUV resist has a thinner thickness than conventional ArF resist and it is more vulnerable to radiation damage received during the etching because of its low etch resistance and also tends to have a problem of low etch selectivity. In this study, the radiation damage to an EUV resist during the etching of hardmask materials such as Si_3N_4 and SiO_2 using a CF_4 neutral beam has been investigated and the results were compared with those etched by a CF_4 ion beam. The results showed, for the etching of the same EUV resist thickness, less line edge roughness, less critical dimension loss, and higher etch selectivity to the hardmask materials such as SiO_2 and Si_3N_4 were obtained for the CF_4 neutral beam etching compared to the CF_4 ion beam etching.

Key word : extreme ultraviolet (EUV) lithography, extreme ultraviolet (EUV) PR, low damage, line edge roughness (LER), critical dimension (CD), neutral beam etching(NBE), ion beam etching(IBE)

9:00am **PS1+NS-TuM-4 Numerical Investigation of EUV Induced H_2-O_2 Plasmas and Surface Chemistry***,* ***Tugba Piskin,*** University of Michigan*; V. Volynets, S. Nam,* Mechatronics Research, Samsung Electronics Co., Ltd, Republic of Korea*; H. Lee,* Mechatronics Research, Samsung Electronics Co., Ltd., Republic of Korea*; M. Kushner,* University of Michigan

Extreme Ultra-Violet (EUV) systems achieve smaller feature sizes in microelectronics processing by deploying photons with ~10 nm wavelength for photolithography. There are several advanced techniques for generating EUV photon beams; one of which is ablating and ionizing tin droplets with pulsed lasers. Excited tin ions emit photons with a 13.5 nm wavelength. These photon beams are collected and focused with a collector mirror, and then photons are transferred to the scanner unit. The lifetime and reflectivity of the collector mirror decline with time due to deposition of tin. An in-situ cleaning technique of tin deposited on the optics involves pumping H_2 into the chamber. H_2 gas does not substantially attenuate the EUV beams, but the photons have enough energy (92 eV) to create an H_2 plasma through photoionization and photodissociation reactions. Hydrogen radicals then etch the tin deposits by producing stannane, a volatile gas which can be pumped from the chamber. The most significant loss mechanism for hydrogen radicals is recombination reactions on the walls. The addition of a small amount of oxygen helps decrease the wall losses of hydrogen radicals by production of the water vapor. The water vapor adsorbs on surface sites, which blocks recombination of H atoms.

In this paper we discuss results from a computational investigation of the low-pressure H_2-O_2 plasma produced from EUV photon beams in a generic EUV photolithography tool using the Hybrid Plasma Equipment Model (HPEM). The densities of radicals, ions, and excited species, their fluxes (including energy-and-angular distributions) to the chamber walls, and the surface coverage fractions will be discussed. For pressures of a few to tens of Pa and hundreds of Watts EUV power, the addition of oxygen increases hydrogen radical density in the chamber and decreases the surface loss of hydrogen radicals. The consequences of oxygen fraction, pressure, and photon intensity on plasma properties and surface mechanisms will be discussed.

Work supported by Samsung Electronics and the National Science Foundation.

9:20am **PS1+NS-TuM-5 Modeling of Shallow Trench Isolation Etch in Self-aligned Double Patterning Process***,* ***Shuo Huang****, P. Panneerchelvam, C. Huard,* KLA Corporation*; S. Sridhar, P. Ventzek,* Tokyo Electron America*; M. Smith,* KLA Corporation

As the critical dimensions (CDs) decrease to a few nanometers while the aspect ratios increase beyond 100, the cost of process development significantly increases and the performance of the plasma etch process is critical to the success of ramping a new technology node toward profitable high-volume manufacturing. In this paper, a plasma dry etch simulator developed at KLA, ProETCH® [1], has been applied to investigate a defect that arises in an overlay metrology target in DRAM during shallow trench isolation (STI) etch patterned using self-aligned double patterning (SADP). SADP process is characterized by performing lithography at a pitch that is two times larger than the desired pitch and is followed by spacer deposition, a spacer etch-back and core etch processes. A challenge of this scheme is that each process introduces some non-uniformity, leading to variations in, for example, the hard mask that is eventually utilized for the final etch. One typical defect is the pitch walk, which manifests different trench openings between the pillars. This periodicity is indicative of the SADP process and corresponds to where the resist core line is patterned initially. The principal objective of this work is to investigate the influence of hard mask irregularities on the STI etch process evolution ProETCH. The mechanism of silicon etch by Ar/Cl_2 plasma was developed with the experimental data (cross-section SEM images) as reference. The variations in the hard mask that arise during the SADP process were found to have a significant impact on the printability of these targets. The differences in trench openings result in aspect ratio dependent etch (ARDE), which could be mitigated by modulating the plasma fluxes to the surface.

[1] P. Panneerchelvam et al., Trilayer hard mark lithography and etch for BEOL manufacturing, SPIE Advanced Lithography, San Jose, California, USA, April 2022.

9:40am **PS1+NS-TuM-6 Polymer Engineering for High Aspect Ratio Plasma Etching Enabled by Chemistry***,* ***Phong Nguyen****, S. Biltek, X. Guo, N. Nathan Stafford,* American Air Liquide

High aspect ratio (HAR) ONON channel etch is a very complex and challenging step in 3DNAND flash memory production and the challenges increase with increasing vertical stack height and reducing pitch sizes. A variety of fluorocarbon gases are used to etch the alternating layers of SiO2 and SiN selective to the mask while maintaining a vertical profile. Control of sidewall polymer formation and its properties such as electrical conductivity are potential pathways to overcome undesirable patterning feature distortions such as bowing, twisting, tilting, and sidewall electrostatic interference i.e "charging."

We demonstrate that engineering the polymer for both its composition as well as conductivity can be accomplished by modification of the chemistry mixture that is used in the plasma process. Characterization of the polymer is done using XPS, SEM, EDS, and current-voltage (I-V) measurements in a variety of simplified test structures to elucidate the properties of the polymer on the etch front and the sidewall. Understanding of the composition of polymers from standard fluorocarbon chemistries including C4F8 and C4F6 along with new fluorocarbons gases will be presented showing changes in the C/F ratio of the polymer on the sidewall at different aspect ratios as well as the difference in polymer between the etch front and the sidewall of test structures. In addition, Quadrupole Mass Spectrometry (QMS), a powerful tool, is implemented to identify positive ion fragments that might be present inside the plasma. Furthermore, such details can elucidate the deposition and etching characteristic of these ions during HAR etching. The combination of polymer characterization and analysis of gas species via QMS can give us a better understanding of the etching process. Finally, new work in improvement of the polymer conductivity using new etching gases will be presented demonstrating >100x improvement in the polymer conductivity.

11:00am **PS1+NS-TuM-10 Achieving Better Etching Performance with Lower GWP Gases***,* ***Nicolas Gosset****, T. Hasegawa, V. Gamaleev,* Air Liquide Laboratories, Japan **INVITED**

Nowadays, new architectures and structures for advanced Logic and Memory devices come with new etching processes and challenges. Among them, anisotropic etching of Si dielectric layers with very high selectivity to the mask, defect free soft-landing to the under layers, and profile control (no bowing, twisting, scalloping, clogging, loss in critical dimensions, and etch stop) is needed for the realization of advanced patterns (e.g. gate spacers, SADP, SAQP, high aspect ratio ONON and contact holes). These layers, such as SiO_2 and SiN, are standardly etched using fluorocarbon-based plasmas that involve multiple simultaneous reactions and phenomena. A key one is passivation, used to suppress lateral etching and damages. Etchants such as CF_4, C_4F_8, C_4F_6, CHF_3, CH_3F, etc. allows the etching of SiO_2 and SiN through the generation of mixed and polymer layers which, assisted by ions bombardment, lead to desorption of volatile byproducts such as CO_x, COF_x, SiF_x, NH_x and HCN. Same polymers generated by these standard gases are also used to protect structure' sidewalls during the etching, where the contribution of ion bombardment is much weaker. Nevertheless, the lack of polymer conformality on the sidewall and its different interactions with the mask or under layer materials strongly contribute to the appearance of etching defects that need to be mitigated.

To mitigate these drawbacks, we investigated the potential of new hydrofluorocarbons-based gases for the etching of high aspect ratio structures, such as 3D NAND holes or DRAM pillars, as well as gate spacers. Not only do these new etchants outperform the ones currently used (higher selectivity to the mask, better profile control, etc.) but they are also more environmentally friendly with lower Global Warming Potentials (GWP). In-depth studies (e.g. polymer deposition, composition, OES, etc.) have shown that these improved performances are linked to the unique polymerization properties of the molecules on the mask and structure sidewalls. The observed differences in profiles etched by two isomers demonstrate the importance and impact not only of the chemical composition but also the molecule structure and design on etch performances. In this example, a first isomer leads to more polymer deposition on the bottom of HAR holes, while polymer generated by a second isomer deposits more on the top. A second example, using a similar approach, demonstrates how the usage of new hydrofluorocarbons in Plasma-Enhanced Atomic Layer Etching process allow reducing SiN spacers footing with a soft-landing on Si channel. Utilizing these lower GWP gases lead to a process with better profile control and similar throughput.

11:40am **PS1+NS-TuM-12 Etch Profile Control for High-Aspect-Ratio Amorphous Carbon Mask Layer Etching**, ***Du Zhang***, *S. Chang, P. Luan, M. Wang,* TEL Technology Center, America, LLC

The etch profile control for the amorphous carbon layer (ACL) is an important step for the 3D NAND fabrication process. Because ACL is the mask material for defining the pattern of the high-aspect-ratio-contact (HARC) dielectric ONON layer etch process, the precise control of its etch profile is necessary. Specifically, an ideal ACL mask profile should be free of symptoms such as hole circularity distortion, profile twisting, bowing, and undercutting. In order to achieve this desired etch performance, knowledge of various etch contributing factors must be systematically derived and applied, including etch surface chemistry, high-aspect-ratio (HAR) etchant transport, ion flux and ion energy angle distribution function (EADF) control, etc.

In this work, we investigate the ACL etch fundamental characteristics through combined 2D chamber-scale plasma simulations with the hybrid plasma-equipment model (HPEM) and 3D etch profile simulations with the Monte-Carlo Feature Profile Model (MCFPM) for an inductively-coupled-plasma (ICP) reactor with RF bias (detailed descriptions of the simulation tools are discussed in M. Wang and M. J. Kushner. J. App. Phys. 107, 023309 (2010)). In particular, we focus on the profile trends under different reactant fluxes and energies. Our findings indicate that maintaining a neutral-starved (ion-rich) etch regime is essential for the mitigation of both the channel hole etch circularity distortion and the slit etch profile twisting. To achieve this desired etch regime, the HAR ion and neutral transport must controlled by the RF bias power and frequency, substrate temperature, etc. Furthermore, especially in this neutral-limited etch regime which is necessary for distortion and twisting mitigation, the control of the consequent aspect-ratio dependent etching (ARDE) as well as maintaining the critical dimension (CD) and reducing bowing and undercutting are also necessary. For this purpose, atomistic density functional theory (DFT) calculations have been applied to compare the reaction energetics for various ALD-like sidewall passivation chemistries. Specifically, we propose a new process based on its favorable reaction energetics. Experimental cross-section images have matched simulation results. In conclusion, our insights have provided guidance for process optimization and tool design to meet the industrial demands.

12:00pm **PS1+NS-TuM-13 A Mask-free and Contactless Plasma Patterning Technique for Interdigitated Back Contact Silicon Heterojunction Solar Cells Fabrication**, ***Junkang Wang***, *M. Ghosh, P. Bulkin, D. Daineka, P. Roca i Cabarrocas,* LPICM-CNRS, École Polytechnique, Institut Polytechnique de Paris, France; *S. Filonovich,* TotalEnergies GRP, France; *J. Alvarez,* Laboratoire de Génie Electrique et Electronique de Paris, CNRS, CentraleSupélec, Université Paris-Saclay, France; *E. V. Johnson,* LPICM-CNRS, École Polytechnique, Institut Polytechnique de Paris, France

Benefiting from the interdigitated back contact (IBC) architecture and the silicon heterojunction (SHJ) technology, IBC-SHJ solar cell currently holds the record efficiency for single-junction solar cells based on crystalline silicon [1]. However, the necessity of performing photolithographic patterning steps to form the interdigitated carrier collection zones makes this architecture unsuitable for low-cost, high-throughput manufacturing processes.

We present here a novel method that allows the creation of the interdigitated carrier collection zones for IBC-SHJ solar cells by PECVD process in a maskless and contactless manner. This method involves using a slottedpowered RF electrode, which has parallel slits in it, in a custom-designed CCP-PECVD chamber. By keeping the RF electrode in close proximity to the substrate surface (down to sub-mm range), plasma will selectively light only within the slits, thus mimicking the patterns on the electrode [2]. Deploying this patterned plasma process with an etching gas mixture (NF_3/Ar) on a well-designed silicon thin film stack, the interdigitated carrier collection zones required for an IBC architecture have been obtained.

Multiple structural and electrical characterizations (profilometry, spectroscopic ellipsometry, photoluminescence, photovoltage mapping, and secondary ion mass spectroscopy) are performed throughout the whole process flow, which gives good guidance for the processes optimization. The J(V) characteristics of the solar cells fabricated by this method will be presented, and the importance of an additional step to remove the damaged layer on the surface left by the patterned etching process will also be discussed.

References

[1] K. Yoshikawa, et al., "Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%", Nat. Energy, 2, 17032 (2017).

[2] R Léal, et al., "Maskless and contactless patterned silicon deposition using a localized PECVD process", Plasma Souces Sci. Tech. 29, 025023 (2020).

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

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

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.

References

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

[2] K. J. Kanarik, S. Tan, W. Yang, I. L. Berry, Y. Pan, and R. A. Gottscho, "Universal Scaling Relationships for Atomic Layer Etching", J. Vac. Sci. Technol. A,**2021**, 39, 010401.

[3] J. R. Vella, D. Humbird, and D. B. Graves, "Molecular Dynamics Study of Silicon Atomic Layer Etching by Chlorine Gas and Argon Ions", J. Vac. Sci. Technol. B,**2022**, 40, 023205.

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, LC **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 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.

[1] Kallol Bera *et al.*, "Influence of inhomogeneous magnetic field on the characteristics of very high frequency capacitively coupled plasmas", ***Journal of Applied Physics***, Volume 107, 053302 (2010).

[2] Jean-Pierre Boeuf, "Rotating Structures in Low Temperature Magnetized Plasmas – Insight from Particle Simulations", ***Frontiers in Physics***, Volume 1, Article 74, 12 December 2014, pp. 1-17.

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.

Atomic Scale Processing Focus Topic
Room 317 - Session AP+PS+TF-TuA

Thermal Atomic Layer Etching

Moderators: Silvia Armini, IMEC, Belgium, **Eric A. Joseph**, IBM Research Division, T.J. Watson Research Center

2:20pm **AP+PS+TF-TuA-1 Thermal Atomic Layer Etching: The Right Etch Technology at the Right Time**, ***Andreas Fischer****, A. Routzahn, R. Gasvoda, J. Sims, T. Lill,* Lam Research Corporation **INVITED**

Thermal atomic layer etching is rapidly becoming an important complementary processing technology in manufacturing of advanced logic and memory semiconductor devices.Critically, stacked chip architectures such as 3D NAND, 3D DRAM or Gate-all-around devices require conformal isotropic etching to remove material such as HfO_2 or SiGe in hard-to-reach locations with aspect ratios that can be greater than 50:1.To achieve repeatable device performance throughout a 3D stack, the removal rate (etch per cycle) of the etched material during an etch process need to be controlled such that the overall etch is the same from top to bottom of the device stack.In this work we studied HfO_2-based 3D NAND test structures with an aspect ratio of more than 50:1. Etching was performed via ligand exchange with dimethyl-aluminum chloride (DMAC) after surfaces had been fluorinated with hydrogen fluoride (HF).Fluorination studies on blanket films revealed that fluorination efficiency is improving for pressures in the Torr range compared to previous millitorr experiments and that only temperatures above 250°C increased the fluorine concentration in HfO_2 significantly whereas fluorine levels were unchanged between 150°C and 250°C.Regarding etch rates in these 3D NAND structures, we found that the horizontal etch rate of HfO_2 as a function of depth (depth loading) depended on the DMAC dosing but was nearly independent on the HF dose.The HF dose and the process pressure were key to increasing the overall etch amount per cycle (EPC).With the highest tested HF dose of 192 Torr*s and a total process pressure of 8 Torr, we achieved a uniform etch amount of 0.6 nm per cycle.In addition, we investigated the impact of film quality and film coating conformality in these structures on the depth loading in the succeeding ALE processes.Type of precursor, precursor dosing, deposition rate as well as substrate temperature played a fundamental role in controlling the film quality and conformality of the deposited HfO_2 layers inside high aspect ratio holes.

3:00pm **AP+PS+TF-TuA-3 Atomic Layer Etching of Titanium Nitride with Surface Modification by Cl Radicals and Rapid Thermal Annealing**, *N. Miyoshi,* Hitachi High Technologies America Inc., Japan*;* ***Nicholas McDowell****,* Hitachi High Technologies America Inc.*; H. Kobayashi,* Hitachi Global Storage Technologies Inc, Japan

Thermal atomic layer etching (ALE) is a promising method for isotropic etching with atomic level precision and high conformality over three-dimensional structures. Due to these characteristics, thermal ALE will be a crucial component of etching the next generation of semiconductor devices. In this study, a thermal ALE process for titanium nitride (TiN) films was developed using surface modification with a Cl2/Ar downstream plasma followed by infrared (IR) annealing of the films. The oxygen-free Cl2-based plasma was adopted to allow a highly selective etch with respect to various materials. Evaluations showed spontaneous etching of TiN during radical exposure can be suppressed at a surface temperature of −10 ºC. Evaluations demonstrated that this process is self-limiting with respect to both radical exposure and IR annealing. With repeated steps of self-limiting radical exposure and IR annealing, TiN was etched at 2.0 nm/cycle, while no thickness change was observed for poly-Si, SiO2, Si3N4, W, and HfO2. The selectivity of amorphous carbon was shown to be higher than 4. X-ray photoelectron spectroscopy analysis showed that the N in the TiN surface layer is spontaneously removed by Cl radical exposure as NClx and NOxCly (Due to residual O in the chamber) species and the film is left with a modified surface layer of TiClx. The remaining TiClx modified layer can then be desorbed by IR annealing, returning the surface layer to its original condition (pristine TiN).

3:20pm **AP+PS+TF-TuA-4 Thermal Atomic Layer Etching (ALE) of Metal Oxides by Chlorination and Ligand Addition using SO_2Cl_2 and Tetramethylethylenediamine (TMEDA)**, ***Jonathan Partridge****, J. Murdzek, S. George,* University of Colorado Boulder

The thermal ALE of many metal oxides, such as Al_2O_3, HfO_2 and ZrO_2, can be accomplished using the fluorination and ligand-exchange mechanism.For other metal oxides, this reaction pathway is not viable because of difficulty finding appropriate ligand-exchange precursors.Fortunately, other etching mechanisms are possible based on ligand addition instead of ligand exchange.During ligand addition, the modified surface layer is volatilized by adding a ligand to the surface metal complex.This study will illustrate the ability of chlorination and ligand addition to etch a variety of first-row transition metal oxides.

Thermal ALE of Fe_2O_3, CoO, NiO and ZnO was demonstrated with sequential exposures of SO_2Cl_2 for chlorination and tetramethylethylenediamine (TMEDA) for ligand addition at 250°C.Using CoO as an example, SO_2Cl_2 chlorinates CoO to form $CoCl_2$ on the CoO surface.TMEDA then undergoes ligand addition with $CoCl_2$ surface species to form a volatile $CoCl_2$(TMEDA) etch product. X-ray reflectivity experiments measured CoO etch rates of 2-3 Å/cycle at 175 - 250°C.The volatile etch products were also identified using a new reactor equipped with a quadrupole mass spectrometer (QMS).The $CoCl_2$(TMEDA) etch product was observed by QMS analysis during TMEDA exposures.CoO etching also involves oxygen loss.Thermochemical calculations indicate that the oxygen could be lost by the formation of SO_3 or O_2.These oxygen products have not been confirmed by QMS analysis.SO_3 is unstable and difficult to observe by QMS.The cracking pattern of SO_2Cl_2 interferes with O_2 detection.

For the other metal oxides, QMS analysis observed $FeCl_2(TMEDA)^+$ ion signals for Fe_2O_3 etching during the TMEDA exposures. $NiCl_2(TMEDA)^+$ ion signals were also monitored for NiO etching during the TMEDA exposures. In addition, $ZnCl(TMEDA)^+$ ion signals were measured for ZnO etching during the TMEDA exposures.Chlorination and ligand-addition was also explored for the thermal ALE of V_2O_5, CuO, Cr_2O_3 and MnO_2. Unfortunately, V_2O_5 and CuO spontaneously etched during the SO_2Cl_2 exposure to form $VOCl_3$ and $CuCl_3$, respectively. Etch products containing TMEDA were not observed for Cr_2O_3 and MnO_2. This work illustrates that sequential exposures of SO_2Cl_2 and TMEDA will be useful for the thermal ALE of a variety of metal oxides that have stable metal chlorides and can not be etched using the fluorination and ligand-exchange mechanism.

4:20pm **AP+PS+TF-TuA-7 Thermal Atomic Layer Etch Processes in Semiconductor Manufacturing Challenges and Opportunities***,* ***Gert Leusink****,* TEL Technology Center, America, LLC **INVITED**

Driven by ever-increasing complexity in materials and structures, process technology requirements in semiconductor device manufacturing have evolved to control at the atomic level. In recent years, atomic level processing has been introduced in deposition, etching, and (wet) cleaning. Chemically selective and/or area-selective processes can be an efficient way to meet future manufacturing requirements[1,2]. Furthermore, damage free low temperature thermal processes will be needed to enable precise control in 3D structures with small CDs and high aspect ratios[3].

In this talk, we will review some of the fundamentals and challenges in thermal Atomic Layer Process technologies for advanced semiconductor device manufacturing. We will discuss recent trends in thermal Atomic Layer Etching (ALE) and show examples how these processes may be used to address some of the critical challenges in cleaning, etching and patterning applications in the manufacturing of 3D devices.

1. *Perspective: New process technologies required for future devices and scaling*, R. Clark [https://aip.scitation.org/author/Clark%2C+R]*et al*, APL Materials 6, (2018)
2. *Overview of atomic layer etching in the semiconductor industry,* Kanarik, K*et al,* Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 33(2), 020802
3. 3-D Self-aligned Stacked NMOS-on-PMOS Nanoribbon Transistors for Continued Moore's Law Scaling, C. -Y. Huang et al, IEDM 2020

5:00pm **AP+PS+TF-TuA-9 Thermal Atomic Layer Etching (ALE) of InGaP:Processing Chemistry and Removal of Surface Defects***,* ***Ross Edel****, T. Nam, S. George,* University of Colorado Boulder

Thermal ALE of crystalline indium gallium phosphide (InGaP) has been developed to extend thermal ALE to phosphide semiconductor materials. These phosphide semiconductor materials are widely used as red light-emitting diode (LED) devices. Native oxides and surface defects on LED devices can lead to electron/hole pair recombination that reduces their light output. In particular, the light output can be significantly reduced on smaller devices having high surface-to-volume ratios. The surface defects are believed to be formed by energetic ion species from previous plasma processing steps. Thermal ALE may provide a method to remove the native oxides and surface defects without causing additional damage.

This work was conducted using a new apparatus that combines a hot wall ALD/ALE reactor with *in vacuo* Auger spectroscopy. This apparatus allows the InGaP sample to be characterized throughout the thermal ALE process without exposure to atmosphere. The thermal InGaP ALE was performed using static, sequential hydrogen fluoride (HF) and dimethylaluminum chloride (DMAC) exposures. The HF/DMAC exposures were able to achieve InGaP etch rates of 0.5–1.0 Å/cycle at temperatures from 300–330 °C, respectively. The etch rates were measured for thin InGaP films on GaAs substrates using *ex situ* spectroscopic ellipsometry.

Etching with only HF/DMAC exposures could produce a chemically distinct top layer. This top layer was believed to be caused by the conversion of the InGaP native oxide to Al_2O_3 or $AlPO_4$ by DMAC. However, this conversion could be avoided by first removing the InGaP native oxide using sequential HF and trimethylaluminum (TMA) exposures. The HF/TMA exposures were able to achieve native oxide etch rates of >1 Å/cycle at temperatures above 300 °C. The underlying InGaP could then be reliably etched with no top layer formation. In the optimized process, the InGaP native oxide was first removed using sequential HF and TMA exposures. Subsequently, the InGaP was etched using sequential HF and DMAC exposures.

The removal of surface defects by ALE was also studied using *ex situ* X-ray photoelectron spectroscopy (XPS). InGaP samples damaged by Ar^+ ion sputtering were analyzed before and after thermal ALE. The XPS analysis focused on the phosphorus XPS signals that revealed the sputter damage. The proportion of the phosphorus XPS signal intensity attributed to sputter damage was found to decrease versus number of thermal ALE cycles.

5:20pm **AP+PS+TF-TuA-10 Thermal Atomic Layer Etching of MoS2 Films**, ***Jake Soares,*** Boise State University; *A. Mane,* Argonne National Laboratory; *S. Hues,* Boise State University; *J. Elam,* Argonne National Laboratory; *E. Graugnard,* Boise State University

2D materials can offer promise for a wide range of application within semiconductor manufacturing. Of these materials, molybdenum disulfide (MoS_2) is of great interest due to its high mobility, measured on/off ratio, tunable band gap, and a film thickness ideal for scaling. In order to move this material closer to integration with semiconductor manufacturing, a great amount of processing control is required. Atomic layer processing techniques can accommodate this needed precision, where both the deposition and removal of MoS_2 has been studied. In this work we report a thermal atomic layer etching (ALE) process for MoS_2 using MoF_6 and H_2O as precursor reactants. Here, we will discuss atomic layer etching of both amorphous as-deposited and crystalline MoS_2 films. In–situ quartz crystal microbalance measurements (QCM) indicate removal of as-deposited films when switching from a deposition chemistry (MoF_6 + H_2S) to the proposed etching chemistry (MoF_6 + H_2O). Saturation curves for the etching process were additionally identified with QCM by studying the mass gained per cycle versus the precursor dose duration. Films deposited on planar coupons were characterized with ellipsometry and X-ray reflectance to determine the etch per cycle. We propose the chemical reaction equations for the etch process as guided by residual gas analysis of byproduct formation, Gibbs free energy calculations, and QCM mass ratio analysis. After ALD and subsequent ALE processing, we produced few layer crystalline MoS_2 films once annealed. With the many application of both amorphous and crystalline MoS_2, this work helps to identify and expand current atomic layer processing chemistries.

5:40pm **AP+PS+TF-TuA-11 Atomically-Precise Surface Processes: From Molecular Mechanisms to Realistic Devices**, ***Andrew Teplyakov,*** University of Delaware

The atomic-level precision in designing surfaces and nanostructures is quickly making its way from the one-off laboratory investigations into chemical manufacturing. However, in order to make the applications feasible, fundamental understanding of the mechanisms of surface reactions leading to the formation of the desired surface structures is needed. A great deal of progress has been made over the years in uncovering reactions behind atomic layer deposition (ALD), but much more limited information is available about atomic layer etching (ALE), although both processes are often required to build the components of present and future microelectronics.

This talk will highlight recent work on understanding the reactions for metal and metal oxide deposition on functionalized (and patterned) surfaces and on recent advances in ALE of complex materials, specifically focused on tertiary alloys, such as CoFeB, used in magnetic tunnel junctions. I will outline the work needed to understand the mechanisms of these processes that can be further used to improve the control over atomically-precise manufacturing methods and to reduce the use of hazardous procedures. The relatively well-understood ALE procedures that include oxidation or chlorination as the first half-cycle of ALE of such materials and introduction of a bidentate ligands (such as acetylacetonates) to remove complex materials uniformly and with atomic-level control will be extended to describe the potential use of much milder conditions and reagents. A combination of experimental and computational methods will be used to make this analysis possible.

6:00pm **AP+PS+TF-TuA-12 Deposit and Etchback Approach for Ultrathin and Continuous Films Using Atomic Layer Deposition and Atomic Layer Etching**, *J. Gertsch, E. Sortino, V. Bright,* ***Steven George,*** University of Colorado Boulder

Ultrathin and continuous films are desirable in many devices such as MIM capacitors and ferroelectric tunnel junctions. Atomic layer deposition (ALD) methods are often used to deposit these ultrathin films. However, nucleation delays can lead to pinholes and thickness variations in ALD films. Higher quality ultrathin and continuous films can be obtained using a deposit and etchback approach using ALD and atomic layer etching (ALE). In this method, an ALD film is deposited to a thickness greater than the desired thickness to reduce the number of pinholes and form a more continuous ALD film. Subsequently, the ALD film is etched back to a smaller thickness using ALE.

The deposit and etchback approach can be illustrated for Al_2O_3 ALD in metal-insulator-metal (MIM) capacitors [1]. The benefit of the deposit and etchback approach can be measured by the percentage yield of MIM capacitors based on an Ag/Al_2O_3/Al structure that do not have an electrical short. Al_2O_3 ALD was performed using sequential exposures of trimethylaluminum (TMA) and H_2O as the reactants. Thermal Al_2O_3 ALE was conducted using sequential exposures of HF and TMA as the reactants. The experiments confirmed that the device yield was improved using the deposition and etchback approach. For example, using device areas of 0.01 mm^2, Al_2O_3 ALD films that were grown to 5 nm in the MIM capacitor displayed a yield of 30-40%. In contrast, Al_2O_3 ALD films that were grown to 24 nm and then etched back to 5 nm to form the MIM capacitor displayed a much higher yield of 65-75%.

Additional experiments revealed that a portion of the yield improvement can be attributed to the fluorination of the Al_2O_3 ALD films [1]. Fluorination produces a volume expansion when forming AlF_3 from Al_2O_3. This volume expansion may produce a compressive stress that helps to close the pinholes. The deposit and etchback approach can also be used to improve the performance of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) ferroelectric tunnel junctions. Thicker HZO films are needed to crystallize HZO films by thermal annealing. However, thinner HZO films are required for the best devices. Recent experiments have shown that the deposit and etchback approach can substantially improve the device performance of HZO ferroelectric tunnel junctions [2].

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[2] M. Hoffmann et al., “Atomic Layer Etching of Ferroelectric Hafnium Zirconium Oxide Thin Films Enables Giant Tunneling Electroresistance”, *Appl. Phys. Lett.* **120**, 122901 (2022).

Plasma Science and Technology Division
Room 305 - Session PS1+TF-TuA

Plasma Processing for Advanced Emerging Memory Technologies, Advanced Packaging and Heterogeneous Integration

Moderators: Hisataka Hayashi, KIOXIA, Japan, **Samson Odunuga**, Intel Corporation

2:20pm **PS1+TF-TuA-1 Study of Residues Formation after Ge-Rich GST Etching Using Halogen Gases**, ***Benjamin Fontaine,*** STMicroelectronics, France; *C. Boixaderas,* Univ. Grenoble Alpes, CEA, Leti, France; *J. Dubois, P. Gouraud, A. Rival,* STMicroelectronics, France; *N. Posseme,* Univ. Grenoble Alpes, CEA, Leti, France

Non-volatile memories patterning is being more and more challenging with dimension reduction. Germanium-antimony-tellurium alloy (GST) has been well studied for phase-change random access memory (PCRAM) applications. Previous publications have proven the interest of using halogen plasmas to etch GST with etch rate range between 200 nm.min^{-1} and 700 nm.min^{-1} using HBr, CF_4 or Cl_2 chemistries. The etching results in halogen implantation in the first nanometers of the material with less modified surface and better roughness using the HBr chemistry. Despite these improvements, complementary analyses recently revealed a defectivity increase (residue formation) after etching and air exposure.

In this work, we propose to study the evolution of the surface state from the first hours of air exposure to several days after the etching using Ge-rich GST full-sheets. We compared the halogen chemistries showing residues formation in the first moments of air exposure after the etching step. Throughout a kinetic study, we showed the criticality of brief air exposures and found the optimal time required for the material protection.We observed a high level of defectivity after 24h of air exposure.

Residues are known for altering devices operation. XPS and EDS analyses revealed that important surface oxidation is present when residues appear. Complementary analyzes revealed that moisture environment has also a catalytic effect on the residue formation. Based on these results, a detailed mechanism responsible of residues formation will be presented.

Using this mechanism, in-situ Post-Etching Treatments (PETs) will be proposed in order to prevent residues formation. We will implement the best PETs on real devices to verify their effectiveness.

2:40pm **PS1+TF-TuA-2 Magnetron Plasma Sputtered $Ge_2Sb_2Se_4Te$ as a Non-Volatile Optical Switch Material***, **Steven Vitale**, P. Miller, P. Robinson, C. Roberts, V. Liberman,* MIT Lincoln Laboratory*; Q. Du, Y. Zhang, C. Popescu, M. Shalaginov, T. Gu,* Massachusetts Institute of Technology*; M. Kang, K. Richardson,* University of Central Florida*; C. Rios,* University of Maryland*; J. Hu,* Massachusetts Institute of Technology

Commercial technologies such as non-volatile memory, integrated photonic circuits, and compact optics are enabled by amorphous-to-crystalline transition of phase change materials (PCMs); for optical applications, the key feature of PCMs is the ability to change the optical properties (n, k) of the material by switching between a high-index crystalline phase and a low index amorphous phase. Here, we study the phase transition of an IR-transparent PCM, $Ge_2Sb_2Se_4Te$ (GSST), deposited using an AJA combinatorial magnetron plasma sputtering system. The film composition was tuned by varying the RF power to each of the Ge, Sb, Te, and $GeSe_2$ sputtering targets based on measurements from an in-situ EDX spectrometer.

Microheaters were fabricated in a fully-depleted silicon-on-insulator technology and coated with GSST. Microheater temperatures in excess of the melting point of GSST (900 K) were achieved. The small mass of the microheater allows for a quenching rate in excess of 10^7 K/s which is critical for amorphization as slower cooling causes recrystallization. The microheater chips were mounted in a Raman microscope and connected to pulsed electronics and the GSST structures was measured after amorphization or recrystallization heater pulses. The characteristic Raman peak of amorphous GSST occurs at 157 cm^{-1} and is consistent with Ge-4Se tetrahedral units. The characteristic Raman peak of crystalline GSST occurs at 120 cm^{-1} and is consistent with Ge-6Se octahedral units. The fundamental crystalline-to-amorphous transition appears to be reduction in Ge coordination from six to four, with the excess selenium atoms forming an amorphous Se-Se network. The amorphous-to-crystalline transition requires breaking the Se-Se network and increasing the Ge coordination from four to six. The measured activation energy for this transition is very close to the Se-Se bond energy and is thus consistent with the proposed mechanism. Enabled by the microsecond heater response we measured an ultrafast time-temperature-transformation diagram for GSST.

No irreversible chemical change (such as oxidation or decomposition) was observed up to 1000 crystallization-amorphization cycles. Lumerical simulations of a telecom-relevant silicon photonic switch show that the measured variation in octahedral/tetrahedral content allows for acceptable insertion loss variability but improved microheater temperature reproducibility will reduce variation in output port contrast.

3:00pm **PS1+TF-TuA-3 Phase-Change Memory Materials Processing Requirements***, **Luxherta Buzi**,* IBM Research Division, T.J. Watson Research Center*; H. Cheng,* Macronix*; M. Hopstaken,* IBM Research Division, T.J. Watson Research Center*; L. Gignac,* IBM Research, T. J. Watson Research Center*; C. Tabachnick, J. Papalia, H. Miyazoe, S. Engelmann, R. Bruce,* IBM Research Division, T.J. Watson Research Center

Switching of Phase Change Memory (PCM) material between crystalline and amorphous phase with electrical pulses and optical properties make it an important candidate for storage class memory and neuromorphic computing [1-2]. These PCM materials (e.g., GeSbTe and its derivatives) can be damaged during plasma etch processing leading to poor performance and yield [3-4]. Surface oxidation of PCM materials can substantially alter switching properties therefore, in-situ encapsulation has been viewed as a favorable solution [5]. It is imperative that RIE and encapsulation mitigate damage or oxidation of PCM material during integration. This paper reviews the effects of etch chemistry, temperature, plasma reactor, and post RIE processing on material properties [3, 6]. In-situ encapsulation of GST and tuning of plasma parameters, caused controlled SiN film deposition with simultaneous selective etching of GST [6]. We have also demonstrated that using alternative chemistry for PECVD film encapsulation can improve GST switching properties and provide a good barrier for GST oxidation.

[1] H. Tsai, et al., Journal of Physics D: Applied Physics, 51, (2018).

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[4] H-Y. Cheng et al 2019 J. Phys. D: Appl. Phys. 52 473002

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3:20pm **PS1+TF-TuA-4 Exploration of Alternative Hard Mask Materials for the IBE Patterning of 50nm Pitch STT-MRAM High Density Orthogonal Pillar Array***, **Romuald Blanc**, L. Souriau, W. Devulder, S. Couet, F. Lazzarino,* IMEC, Belgium

In order to approach the bit density of dynamic random access memory (DRAM), spin-transfer torque (STT) magnetic random access memory (MRAM) requires to be scaled down to pitch 50nm and below[1,2]. To fabricate 50nm pitch STT-MRAM high density pillars, ion beam etching (IBE) is used to pattern the magnetic-tunneling junction (MTJ). This etch technique relies mainly on physical ion sputtering which does not allow high selectivity to the hard mask[3], therefore a robust material is needed to avoid excessively thick hard mask and high pillar aspect ratio.

In this talk, we present the etch rate of multiple materials deposited in 300mm production tools etched with different with ion beam etching conditions. Then we demonstrate the patterning of a hybrid hard mask composed of high-density diamond-like carbon (DLC) to increase etch selectivity and TiN which will become the STT-RAM top electrode. Finally, the interest of this hybrid DLC/TiN hard mask is evaluated for the patterning of the MTJ stack with IBE.

References:

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

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

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4:20pm **PS1+TF-TuA-7 Patterning Approaches for Integration of Complex Metal Alloys Towards Advanced Memory and Compute Applications***, **Shreya Kundu**, F. Lazzarino,* IMEC, Belgium **INVITED**

Increasing need of data processing from core electronic devices is instrumental in driving the innovation of high-density memories and high-performance computing in the semiconductor industry. To sustain this growth in storage and computing domains, novel material systems are being investigated exhaustively due to their promising intrinsic properties. A key challenge here is their satisfactory patterning to enable assimilation into integrated chips.

Patterning studies of complex alloy systems generally aim at finding a suitable etch chemistry which promises good feature profiles with minimal physical and chemical damage. However, when integrated with diverse electrode materials (for e.g. SiN, TiN), it becomes imperative for the patterning investigation to include an additional criterion i.e., the etching of the novel alloy or the electrode should not have an adverse morphological or structural impact on one another, as it can lead to poor electrical performance. Patterning of two types of complex material systems – chalcogenide-based films (GeSbTe, SiGeAsTe/Se) and InGaZnO (IGZO) – displaying etching attributes on opposite ends of the spectrum are discussed here. Chalcogenides find widespread application in resistive, holographic non-volatile memory, and ovonic threshold switches due to their unique electronic and optical response signatures. Therefore, these materials are often integrated with optically conductive electrodes and heat sinks within an electrical circuit[1]. As chalcogenides produce highly volatile halogen-based by-products[2], prolonged exposure to similar etchants used in conventional electrode patterning schemes can cause severe undercuts leading to feature collapse. On the other hand, IGZO, a potential candidate for high performing thin film transistors[3], can be patterned using a hydrocarbon etchant and remains unimpacted by the chemistries used for etching electrode materials[4]. However, IGZO-based residues along electrode sidewalls are common post-patterning, thereby making the devices prone to current leakage.

In this talk, an overview of challenges encountered in patterning complex materials in varied integration schemes is presented followed by a systematic discussion on etch approaches to circumvent them. The repeatability and scalability of the etching schemes are also discussed.

Acknowledgments- to IMEC's Industrial Affiliation Program, IMEC's Active Memory and TIP integration team.

References

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5:00pm **PS1+TF-TuA-9 Plasma Etch Challenges and Processing Optimization in Spin Logic Device Fabrication***, **Yann Canvel**, L. Souriau,* IMEC, Belgium

Presently, microprocessor chips rely on the networking of billions of tiny switches, commonly called transistors. These CMOS-based technologies run logic operations via the electron charge to enable data computing for the function of any digital object. In the development of next-generation logic devices, an alternative solution would be to leverage the electron's spin instead of the electron's charge. This specific electron manipulation paves the way towards the fabrication of spin logic devices which promises high performances and low power consumption.

In this communication, close attention will be dedicated to the unique patterning challenges of such architectures. It mainly consists of creating a magnetic interconnect system to propagate, in a controlled way, the information through the magnetic logic circuit. Ion Beam Etch (IBE) technique is used to shape the magnetic track. The critical point is to control the vertical etch of the Magnetic Tunnel Junction (MTJ) stack at nanometric scale. In this frame, a deep understanding of the plasma-surface interaction is required and will be presented here. As a result, some process optimization will be discussed to mitigate the ion-induced damages. Both soft landing and cyclic IBE approaches will be highlighted as proof of concept.

Raymenants, E. *et al.* Nanoscale domain wall devices with magnetic tunnel junction read and write. *Nat Electron***4**, 392–398 (2021).

Raymenants, E. *et al.* All-Electrical Control of Scaled Spin Logic Devices Based on Domain Wall Motion. *IEEE Trans. Electron Devices***68**, 2116–2122 (2021).

Raymenants, E. *et al.* Magnetic domain walls: from physics to devices. in *2021 IEEE International Electron Devices Meeting (IEDM)* 32.3.1-32.3.4 (IEEE, 2021).

5:20pm **PS1+TF-TuA-10 Effects of Bias Frequency on High Aspect Ratio Etching Using Voltage Waveform Tailoring***, **Florian Krüger**,* University of Michigan*; H. Lee, S. Nam,* Mechatronics Research, Samsung Electronics Co., Ltd., Republic of Korea*; M. Kushner,* University of Michigan

The continuing reduction of feature sizes and increasingly high aspect ratios (HAR) in plasma etching pose major challenges to high volume manufacturing of nanoscale semiconductor devices. Capacitively coupled plasmas (CCPs) are an important tool for HAR etch processes. In these systems, the DC self-bias is used as a measure of mean ion energies incident onto the wafer. DC bias is coupled to the asymmetry of the system which can be a function of geometry, material differences, magnetic configurations and the use of non-sinusoidal voltage waveform tailoring (VWT) through the electrical asymmetry effect.

We computationally investigated the consequences of bias frequency on ion energy distributions (IEDs) and SiO_2 etch properties when varying the electrical asymmetry of the bias waveform.The electrical asymmetry is controlled with the phase shift of the even harmonics ϕ of a multifrequency waveform.The system is a CCP with high frequency source power and low frequency bias power.The plasma was sustained in fluorocarbon gas mixtures at 40 mTorr. The bias waveform consisted of 5 harmonics with a base frequency of 1 to 10 MHz. The gas phase simulations were performed using the Hybrid Plasma Equipment Model (HPEM).Using reactive fluxes to the wafer from the HPEM, etching of a HAR via in SiO_2 was simulated using the Monte Carlo Feature Profile Model.The resulting features were evaluated based on etch rate, etch depth and distortion.

We found that at sufficiently high bias frequencies where ions are unable to react to time-varying fields in the sheath, IEDs are dominantly affected by time-averaged sheath electric fields. Mean ion energy is correlated to the DC self-bias, which in turn is correlated to **ϕ.** In this regime maximumion energies occur when ϕ=0, and electrical asymmetry as well as DC self-bias magnitude are maximum. The resulting etch features have most desirable qualities when ion energies are high at low phase angle.

This trend does not apply and, in fact, reverses for low bias frequencies where ions are able to dynamically react to transient electric fields. This leads to temporal variations in ion energies and fluxes which result in higher ion energies at higher phase angles and lower electrical asymmetry. The trend of reversal in ion energies with phase angle also translates to the etch feature having better overall quality at high phase angle. We conclude that when using VWT techniques for process control in etch systems, there are two frequency regimes (dynamic-ions and stationary-ions) having different control mechanisms.

Work supported by Samsung Electronics and the National Science Foundation.

5:40pm **PS1+TF-TuA-11 Wafer Bevel Deposition by Localized SiO_2 and Si_3N_4 PECVD and Application to 3D Integration***, **Francois Boulard**, F. Fournel, V. Lapras, L. Brunet, D. Truffier-Boutry,* CEA-University Grenoble Alps, France*; P. Ruault,* Lam Research, France*; M. Keovisai,* Lam Research*; C. Porzier, V. Gros, N. Posseme,* CEA-University Grenoble Alps, France

As 3D integration schemes move forward new process challenges arise. One of them is to manage contamination issues of multiples stacked wafers. Particularly, wafers edge and bevel are known to be the source of delamination or defects, as metals or particles contaminations[1-3]. This is even more critical after bonding when back-end of line wafers are reprocessed on front-end tools[4]. In this paper, we present a strategy consisting in encapsulating the bevel area in a single process step. SiO_2 and Si_3N_4 are deposited by PECVD at 350°C on blanket 300mm Si and CMOS + 4 BEOL levels wafers. We study the influence of pressure, RF power, and single or dual frequency plasma excitation on deposition rate, refractive indexes, and films stoichiometries by XPS. No deposition occurs on most of the top surface since the gap between the wafer front side and the top grounded electrode remains below 1 mm. On the wafer edge and bevel, where plasma and deposition take place, films wet etch rates confirm oxide and nitride excellent qualities. The radial deposition profiles is characterized by ellipsometry and scanning electron microscopy cross section. The integration of bevel deposition on CMOS+M4 products is studied. We demonstrate the compatibility of the approach with top tier bonding and the effectiveness of the encapsulation to control BEOL metal contamination.

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[https://www.scopus.com/sourceid/26142?origin=resultslist], 2018-December,8614653, pp. 7.2.1-7.2.4

6:00pm **PS1+TF-TuA-12 Plasma Etching of Copper for the Microfabrication of High-Density Interconnects in Advanced Packaging*, Juliano Borges*, *M. Darnon, Y. Beilliard, D. Drouin,* Université de Sherbrooke, Canada**

Low-cost and high-density redistribution layers (RDL) in integrated circuits packaging are essential to support further development in the fields of high-performance computing and internet of things. Indeed, both require low-cost electronic systems capable of delivering higher bandwidths, improved operation speeds, and enhanced power performance, which can be done by in-package multi-chiplets interconnection.

Organic or silicon interposers have been developed to allow the connection of dies in 2D configurations. Even if silicon-based interposers offer the best interconnects density, they cannot be used in high-frequency applications due to the high resistive losses induced by silicon and their cost is prohibitive for consumer electronics applications. High-density RDL fabrication on organic interposers is therefore required for high-frequency operation and low-cost manufacturing. However, conventional organic interposer fabrication methods by semi-additive processes are not compatible with high-density RDL (<2 µm pitch) because of isotropic wet etching of the seed layer. On the other hand, damascene processes cannot be performed on organic substrates because of substrate warpage. We propose to revisit copper etching processes for high-density RDL fabrication on organic substrates.

Chlorine-based plasmas have been explored as an alternative for etching copper, generally employing cyclic approaches. $CuCl_2$ species are formed upon exposure to Cl radicals and can be transformed into volatile Cu_3Cl_3 when exposed to hydrogen [1]. We developed a one-step $Ar/Cl_2/H_2$-based plasma in an inductively coupled plasma (ICP) chamber with a cathode temperature of 200°C. Using this process, we demonstrated the anisotropic plasma etching of copper with an etch rate of 500 nm/min. A specific seasoning and cleaning process was also set up to provide reproducible etching conditions with no significant chamber contamination after cleaning. By optimizing the etch process, we were able to fabricate high-density copper-based RDL with a pitch of 2 µm. Preliminary tests validated the compatibility of the process with organic substrates.

These results demonstrate the capability of plasma etching processes to etch copper for the fabrication of high-density RDL on an organic substrate for advanced packaging applications.

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Plasma Science and Technology Division
Room 315 - Session PS2+AS+SS-TuA

Plasma-Surface Interactions

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

2:20pm **PS2+AS+SS-TuA-1 Selective Mask Deposition Using $SiCl_4$ Plasma for a Highly Selective Etching Process*, Miyako Matsui,*** Hitachi Ltd., Japan*; K. Kuwahara,* Hitachi High-Tech Corp., Japan **INVITED**

The local cell size of logic devices has been continuously shrinking at a scaling rate of about 0.48 per 2 years. Extreme ultraviolet (EUV) lithography is a key technology for pitch scaling, though the pitch scaling rate has been slowing down since 2010. To boost the scaling, design technology co-optimization (DTCO) has been developed by using various kinds of self-aligned processes. However, process challenges exist for both technologies. Etching processes using thin EUV resists require extremely high selectivity and precise control of critical dimensions. Selective etchings for DTCO require high selectivity between layers having a similar material composition. In both cases, selective deposition for forming protective layers only on unetched materials can solve these process challenges and achieve extremely highly selective etchings.

In this study, we investigated a selective deposition process for forming protective layers on top of masks generated by a microwave-ECR etching system. A deposition layer was formed only on SiO_2 masks without forming an unnecessary deposition layer on Si surfaces of etching area, such as bottoms of the patterns and isolated etching area. This process effectively achieves extremely highly selective etchings by selectively forming the protective layers prior to the etching procedure in the same chamber.

We suggested a process for selectively forming protective layers on a SiO_2 without forming on a Si etching area by using a $SiCl_4/H_2/Cl_2$ plasma. Top surfaces of the materials needed to be cleaned before forming the protective layer. Selectivity is thought to be provided by the difference in $SiCl_x$ desorption processes. On the Si surface, adsorbed $SiCl_x$ easily desorbed again by reacting with Cl generated from the plasma. On the other hand, adsorbed $SiCl_x$ on SiO_2 was thought to be more difficult to desorb by reacting with Cl due to Si-O having larger binding energy than Si-Si. After the deposition layer was selectively formed on the SiO_2 mask, the layer was oxidized using an O_2 plasma treatment to improve the etching resistance during the Si-etching. The O_2 plasma treatment time was controlled not to prevent the Si substrate from being etched during the Si-etching. We found the optimum O/Si concentration of oxidized protective layer was about 0.4 from X-ray photoelectron spectra (XPS) analysis.

We also demonstrated the selective deposition to etch a line-and-space pattern with a SiO_2 mask. In this process, selective deposition, oxidation, and Si etching were cyclically carried out. The extremely highly selective etching was achieved using the selective deposition without forming an unnecessary deposition on an isolated Si area.

3:00pm **PS2+AS+SS-TuA-3 On the Self-bias Voltages at Sintered Yttrium Oxyfluoride (Y-O-F) and Y_2O_3 During Plasma Irradiation and Their Etching Rates due to Ion Bombardment*, Tetsuya Goto*,** *Y. Shiba,* Tohoku University, Japan*; A. Teramoto,* Hiroshima University, Japan*; Y. Kishi,* Nippon Yttrium Co., Ltd, Japan*; S. Sugawa,* Tohoku University, Japan

Yttrium oxyfluoride (Y-O-F) has been received much attention as the bulk and/or coating materials for functional components used in the plasma process chamber in semiconductor manufacturing, because chemical component stability of Y-O-F against various corrosive plasmas is better than that of widely used Y_2O_3 [1-3]. In addition to the chemical component stability, etching rate of these materials is also an important issue when particle problem and lifetime of the components are considered in industry. Previous report has shown that the etching rate of Y-O-F and Y_2O_3 due to plasma irradiation is almost the same level [2]. On the other hand, we reported that, the etching rates of the sintered Y-O-F due to the Ar ion beam irradiation (without plasma) was clearly smaller than that of Y_2O_3 [3]. We speculated that such tendency was caused by higher atomic number density of Y-O-F than that of Y_2O_3. Thus, the etching behavior of Y-O-F and Y_2O_3 was different between the cases of the ion beam irradiation and the plasma irradiation.

In this report, to understand the observed difference in more detail, we measured self-bias voltage V_{dc} of surfaces of Y-O-F and Y_2O_3 samples set on Si wafer in 13.56-MHz excited capacitive coupling Ar plasma. Here, V_{dc}, which is approximately an acceleration voltage of ions, is a good parameter to estimate ion bombardment energy at the sample surface. It was found that $|V_{dc}|$ of Y_2O_3 was smaller than that of Y-O-F, suggesting that surface voltage condition was different under the normal setup of the samples for the plasma irradiation test. In this setup, etching rates of Y-O-F and Y_2O_3 due to Ar plasma irradiation were found to be almost the same.

Next, to equalize the surface voltages of Y_2O_3 and Y-O-F during the plasma irradiation as far as possible, we connected the sample surface and the Si wafer surface using electrically-conductive carbon tape. In this case, it was found that the etching rate of Y-O-F was smaller than that of Y_2O_3, showing the same behavior to the Ar ion beam etching experiment.

The results suggested that the intrinsic etching resistance of Y-O-F due to the ion bombardment is better than that of Y_2O_3. Also, the results showed the importance of how the sample was set in the plasma irradiation test to accurately estimate plasma resistance. Furthermore, it is considered that, in the actual plasma equipment, plasma resistance depends strongly on how the protect material was set or coated.

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2. H. Ashizawa and K. Yoshida, Int J Appl Ceram Technol. (2021) 1.
3. T. Goto et al., J. Vac. Sci. Technol. A, 38 (2020) 043003.

4:20pm **PS2+AS+SS-TuA-7 In-Plasma Photo-Assisted Etching of Si with Chlorine Aided by an External Vacuum Ultraviolet Source***, L. Du, D. Economou, **Vincent M Donnelly,*** University of Houston

Photo-assisted etching (PAE) of *p*-type Si(100) was found to occur in a chlorine-containing, Faraday-shielded, inductively coupled plasma (ICP) with no substrate bias, attributed mainly to the vacuum ultraviolet (VUV) light generated by the plasma. Other causes for the very high etching rates can be ruled out, including ion bombardment-assisted etching and chemical etching by Cl atoms. Masked samples produced slow etching (111) facets and smooth surfaces. To provide additional evidence for the VUV-PAE mechanism, the substrate in a main Cl_2/Ar ICP was subjected to extra VUV light (mainly 104 and 106 nm Ar emission) that was generated in an independently controlled, auxiliary Ar/He ICP in tandem with the main ICP. The ICPs were separated by a tungsten mesh and a bundle of high-aspect-ratio quartz tubes in a honeycomb configuration. There was no measurable perturbation of the main plasma by the auxiliary plasma. The etching rate was found to be enhanced by 11 to 51% with the additional VUV light provided by the auxiliary ICP. Absolute measurements of the auxiliary ICP photon flux at the surface were obtained in-situ by recording photoemission yields from a Au-coated sample in place of the Si substrate. Incredibly large etching yields of 90 to 240 Si atoms-per-photon were obtained. It is argued that etching is not a result of electron-hole pair formation, but is instead ascribed to a photo-catalytic chain reaction. No etching occurs with just $Cl_{2(g)}$ and the auxiliary VUV source, hence Cl atoms produced by the main ICP are required to produce the more highly chlorinated surface required for propagation of the chain reaction.

4:40pm **PS2+AS+SS-TuA-8 Etching of Silicon Dioxide (SiO_2) Based on Remote Plasma-Based Functionalization and Electron Beam-Activation***, **Yudong Li**, K. Lin,* University of Maryland, College Park*; C. Preischl, C. Hermanns, D. Rhinow, H. Solowan, M. Budach, H. Marbach, K. Edinger,* Carl Zeiss SMT, Germany*; G. Oehrlein,* University of Maryland, College Park

Electron-beam stimulated activation of SiO_2 surfaces functionalized by remote plasma is demonstrated as a promising novel approach to achieve atomic scale etching. Compared to conventional plasma-based dry etching utilizing ion bombardment, electron-beam induced etching (EBIE) avoids ion-induced damage effects such as atomic displacement and atomic mixing. One issue with EBIE is the limited number of chemical precursors that is available to functionalize substrate surfaces without spontaneous etching.

In this work, we demonstrate a new approach that combines surface functionalization by a remote plasma source and energy deposition using an electron beam source to enable EBIE. A prototypical case is SiO_2 etching using Ar/CF_4/O_2remote plasma generated precursors and electron-beam initiated removal of the chemically reacted surface layer by low-energy electron bombardment. We evaluated the parametric dependence of SiO_2etching on remote plasma source and electron flood gun operating parameters, including radiofrequency (RF) source power, CF_4/O_2 flow composition, electron energy and emission current, respectively. Two prototypical processing cases were examined: one simultaneous and two sequential remote plasma treatment and electron beam irradiation. Material selective atomic scale etching of Si_3N_4 over SiO_2 and poly-Si over SiO_2 were demonstrated. Surface chemcial modification and etching were followed by in-situ ellipsometry measurements. Surface chemical changes were also characterized by x-ray photoelectron spectroscopy and revealed mechanistic insights for these processes.

We gratefully acknowledge the financial support of this work by ZEISS SMT GmbH.

5:00pm **PS2+AS+SS-TuA-9 Investigation of Plasma-Surface Interactions During Plasma Enhanced Atomic Layer Deposition (PE-ALD) of Silicon Nitride Using *in Situ* Surface Chemistry Measurements***, **Samuel Johnson,*** University of Texas at Austin*; J. Zhao, T. Iwao, J. Carroll, C. Schlechte, P. Ventzek,* Tokyo Electron America*; J. Ekerdt,* University of Texas at Austin

A low temperature process for silicon dielectric thin film deposition is necessary for a wide range of semiconductor process applications, including as spacers in FinFET and self-aligned multiple patterning. Using plasma enhanced atomic layer deposition (PE-ALD) with radio frequency (RF) power to deposit silicon nitride films is very promising as it lowers the deposition temperature compared to thermal atomic layer deposition; however, direct plasma enhanced processes face a difficulty of guaranteeing the conformality of film thickness and film properties on high aspect ratio, 3-dimensional device structures. Ionized plasma species have a high degree of directionality, resulting in differences between top facing and sidewall surface coverage and properties. Ion beam incoherency, which can be tuned by varying the frequency and pressure, may be used to achieve more property conformity.

To explore the PE-ALD of silicon nitride, we built a radio frequency capacitively-coupled plasma (CCP) PE-ALD chamber.Our PE-ALD process involves one half cycle of dichlorosilane (DCS) gas for silicon layer adsorption, and another half cycle of an ammonia/argon plasma for nitridation. We used three different RF frequencies in deposition experiments on planar surfaces and a 3-dimensional trench-patterned surface in a silicon substrate. We have investigated the bulk film and surface chemistry using *in situ* X-ray photoelectron spectroscopy (XPS) and *in situ* Fourier-transform infrared spectroscopy (FTIR). With increasing frequency, the overall N-H_x bonding decreased (a higher percentage of nitrogen bonds were unsaturated), and the remaining N-H_x bonds became rich in N-H_2 bonds compared to N-H bonds. Further details will be discussed on the correlations between the plasma characteristics (ion energy and angle, neutral flux, etc.), the *in situ* surface chemistry measurements, and the film properties.

5:20pm **PS2+AS+SS-TuA-10 Differences in Sidewall Chemistry for SiO_2 and Si_3N_4 after Ar/HFC or Ar/FC Plasma Processing Using High Aspect Ratio Structures***, **Sang-Jin Chung,*** University of Maryland, College Park*; P. Luan, A. Metz, M. Park,* TEL Technology Center, America, LLC, USA*; G. Oehrlein,* University of Maryland, College Park

State-of-the-art 3-dimensional memory devices utilize high-aspect-ratio (HAR) heterogeneous structures where 2 or more materials are etched simultaneously during the fabrication process. Controlling the sidewall chemistry of stacked materials etched using the same fluorocarbon (FC) or hydrofluorocarbon (HFC) process is one of the key factors for yielding excellent etch profiles. Here, we use a horizontal trench gap structure [1,2] to simulate the interaction of neutral radicals produced by FC and HFC plasma with SiO_2 and Si_3N_4 sidewalls in HAR structures for aspect ratios (AR) of up to 90. Oxide and nitride trench structures were simultaneously treated with Ar/FC or Ar/HFC plasma without RF bias and changes in film thickness were probed by ellipsometry as a function of AR. We find a variety of responses of the trench sidewalls for the remote plasma conditions, including both polymer deposition and spontaneous etching. These responses are dependent on the type of FC and HFC gases, the surfaces being exposed, and the position relative to the trench entrance. For HFC chemistry, oxide shows relatively little etching near the trench entrance followed by the presence of a very thin FC layer (<1 nm) for increasing AR. For the same conditions Si_3N_4 shows significantly more etching both near the entrance and for high AR deep in the structure. For FC plasma the behavior is different and polymer deposition is primarily seen for the high-AR trench structures. These observed behaviors are further correlated to the scalloping phenomenon commonly seen in layered ONO HAR structures. We will also discuss the surface responses with in-situ characterizations, including optical emission spectroscopy (OES), and FC deposition rate measurements seen for directly exposed SiO_2 or Si_3N_4 surfaces.

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5:40pm **PS2+AS+SS-TuA-11 Significance of Plasma-Surface Interactions in the Etch Behavior of Low-k Materials*, Adam Pranda,*** *S. Grzeskowiak, Y. Yoshida, E. Liu, Y. Han, P. Biolsi,* TEL Technology Center, America, LLC*; K. Kobayashi, N. Ikezawa,* Tokyo Electron Miyagi Ltd., Japan

Low-k materials are an integral component in the advancement of semiconductor device performance by reducing parasitic capacitance and enabling faster device switching for a given thickness compared to traditional dielectric materials such as SiO_2. With the advances in logic scaling, low-k materials are increasingly more prominent in the structures of advanced devices. For example, low-k materials are being targeted as the inner spacer ingate-all-around (GAA) nanosheet field effect transistors. Consequently, the integration of low-k materials requires that the etch behavior of these materials be well understood so that the device structures can be reliably and reproducibly fabricated. In this study, we used a high-density plasma reactor with benchmark CF_4- and NF_3-based process chemistries to etch low-k materials including SiCN, SiOCN, and SiBCN along with reference materials including Si, SiO_2, and SiN. We utilized a characterization suite consisting of optical emission spectroscopy (OES), mass spectroscopy (MS), spectroscopic ellipsometry (SE), x-ray photoelectron spectroscopy (XPS), and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to understand the relationships between the plasma conditions (OES, MS), the evolution of the surface chemistry of the materials (XPS, ATR-FTIR), and the resulting etch behavior (SE). The etch behavior of low-k materials under a given etch process is vital for establishing the etch selectivities in multilayer structures that are required to yield complex device geometries. For example, we found a correlation in the relative magnitude of OES trend for the CN emission at 387nm to the low-k material etch rate, which suggests that preferential sputtering of the nitrogen and possibly carbon from the sample is one of the main pathways for the etching of nitrogen-containing low-k materials. Identifying the underlying mechanisms for the etch behaviors of low-k materials will provide key guidance into the development of etch processes that integrate these materials in current and future device structures.

6:00pm **PS2+AS+SS-TuA-12 Low Temperature Superpermeability in Metal Foils Exposed to Hydrogen Plasma***, **Chao Li**, A. Job,* Colorado School of Mines*; M. Shimada, T. Fuerst,* Idaho National Laboratory*; D. Way, C. Wolden,* Colorado School of Mines

The hydrogen isotopes tritium (T) and deuterium (D) are leading fuels for use in future fusion reactors. In these reactors they combine to form He and an energetic neutron in a high density, magnetically confined plasma. Metal foil pumps are a technology to extract the unreacted isotopes from the He ash in the plasma exhaust and return them to the plasma in a process known as direct internal recycling. Hydrogen separation membranes typically work through a dissociative adsorption - atomic diffusion - recombinative desorption mechanism that relies on a hydrogen partial pressure gradient. Unlike molecular hydrogen, energetic H atoms and ions can bypass the dissociation/absorption step and directly enter the metal. This leads to hydrogen fluxes that can be orders of magnitude greater than expected from Sievert's law, a condition described as superpermeability. In this study, we investigate the superpermeability of various metal foils (PdAg, V and α-Fe) exposed to inductively coupled H_2 plasma operating at low temperature (50-200 ^{o}C) and the results are compared to a fundamental model accounting for individual steps in hydrogen permeation. Systematic variation of foil temperature and plasma parameters were used to illuminate the key rate limiting steps in the mechanism. Interfacial treatments including oxidation, plasma cleaning, and the deposition of nanoscale interfacial layers were used to modify surfaces to improve the hydrogen permeation of metal foils. Auger and AFM characterization were used to study the surface elemental composition and metal surface roughness, respectively. Both H_2 and D_2 plasmas were employed to better understand isotope effects. V foils with symmetric Pd deposition on both sides showed comparable permeation performance to PdAg foil with hydrogen flux exceeding 10^{20} m^{-2} s^{-1}. On the other hand, plain α-Fe foils showed very stable, but lower (10^{19} m^{-2} s^{-1}) hydrogen flux performance in repeated tests. Our findings suggest that V and α-Fe with appropriate surface modification are promising candidates for use as metal foil pumps for direct internal recycling of DT fuels in future fusion reactors.

Plasma Science and Technology Division
Room Ballroom A - Session PS-TuP
Plasma Science and Technology Poster Session

PS-TuP-1 SiO_2 Contact Hole Etching Using Heptafluoropropyl Methyl Ether Plasmas*, **Sanghyun You**, C. Kim,* Ajou University, Republic of Korea

Perfluoro carbons (PFCs) such as CF_4 and c-C_4F_8 are mainly for SiO_2 etching. PFCs aggravate global warming even in small amounts due to their high global warming potentials (GWPs). As the critical dimension keeps decreasing, the number of processes consisting of etching-deposition repetition such as double patterning technology increases, leading to an increase in PFC emission. According to the World Semiconductor Council, the emission of PFCs from the global semiconductor processes in 2020 has been increased by 37.9% compared to that in 2012. Semiconductor industries are trying to reduce PFC emissions through post-treatment processes such as recovery or decomposition of exhaust gases. However, it is not suitable as a long-term solution since a lot of electricity or water is used in the post-treatment processes. To reduce PFC emission from a long-term perspective, it is necessary to develop a process using materials with low GWPs. Unsaturated fluorocarbons, iodofluorocarbons, fluoroethers, and fluoroalcohols have been studied as alternative chemistries to PFCs.

In this study, SiO_2 contact hole etching was conducted using heptafluoropropyl methyl ether (HFE-347mcc3) plasmas. HFE-347mcc3 belongs to fluoroethers, and its GWP (~350) is significantly lower than that of PFC. The angular dependence of the SiO_2 etch rates were investigated to explain the etch mechanism during SiO_2 contact hole etching.

PS-TuP-2 Selective Cyclic Etching of Silicon Oxide Over Silicon Nitride Using NF_3/H_2 Remote Plasma and NH_3*, **Hong Seong Gil**, Y. Gill, D. Kim, Y. Jang, H. Kwon, D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

For the selective isotropic etching of SiO_2 over Si_3N_4, due to the pattern sticking by a capillary action in nanoscale patterns, dry etch processing methods are widely investigated instead of wet etch processing especially for the next-generation semiconductor processing. Among various isotropic dry etching methods using plasmas, combinations of F-based gases and H-based reactive gases, such as NF_3/NH_3, OF_2/NH_3, CF_4/ NH_3, etc. have been investigated with downstream plasmas, remote plasmas, and so forth. In addition, these days, for the applications to various semiconductor devices, it is found that it is necessary to control the thickness of etched oxide thickness during the etching in addition to improving high selectivity over silicon nitride. In this study, selective isotropic cyclic dry etching of silicon oxide (SiO_2) was investigated using a three-step cyclic process composed of hydrogen fluoride (HF) adsorption by NF_3/H_2 remote plasma, reaction with NH_3 gas flow to form ammonium fluorosilicate ($(NH_4)_2SiF_6$), and desorption by heating. The variation of the ratio of NF_3:H_2 and adsorption time showed the variation of etch selectivity of SiO_2 over Si_3N_4. The characteristics of the cyclic remote plasma etching by NF_3/H_2 gas chemistry were analyzed by FT-IR and, the etch depth per cycle and etch profiles of SiO_2 were observed by an ellipsometer and FE-SEM.

PS-TuP-3 Identification of Critical Factors in Plasma Enhanced Atomic Layer Etching of Silicon Nitride through First-Principles-Based Simulations*, **Erik Cheng**, G. Hwang,* The University of Texas at Austin*; P. Ventzek, Z. Chen, S. Sridhar,* Tokyo Electron America

Viable plasma enhanced atomic layer etching (PEALE) of silicon nitride (SiN) by inert ion bombardment of a hydrofluorocarbon (HFC) treated surface has been demonstrated, but the details of the underlying mechanisms remain poorly understood. To this end, we have used molecular dynamics (MD) simulations based on the self-consistent-charge density-functional tight-binding (SCC-DFTB) theory to study the nonequilibrium chemistry and physics that can occur during PEALE of SiN with HFCs. From analyzing the results of thousands of such simulations, we have identified several potentially critical factors for the design of improved PEALE processes to be used in next-generation semiconductor manufacturing.

We first assessed the reactivity of surfaces, both with and without ion damage, and found it to be generally unreactive towards HFCs, suggesting that HFCs may primarily stay physisorbed, rather than chemisorbed, prior to ion bombardment.

Secondly, these physisorbed HFCs, upon ion bombardment, produce key decomposition fragments that may dictate the nature of the chemical modification that is achieved in the underlying film. This is seen when comparing CF4 and CH3F, the former primarily decomposing to CF2 and 2F while the latter decomposes to CH3 and F. As a result, CF4 results in greater amounts of F modification in the film, a tendency for C atoms forming higher order bonds with atoms in the film, and greater ion penetration depth.

Thirdly, we find that the nature of the film modification in PEALE is not only a function of NC and SiF bond formation, but that further SiC bond formation and defect generation in the film also have a major influence and may be important for volatilization of etch products. These etch products not only tend to contain F, but also H, C, and N, although to a lesser extent. However, at greater concentrations, we have demonstrated that F continues to be beneficial for volatilization, but that C and H can have adverse and neutral effects, respectively.

Our simulations have demonstrated the key roles of the complex dynamics induced by ion bombardment during PEALE, and we have highlighted key aspects identified from our analyses. Through understanding these key influences, development of improved PEALE processes could be greatly accelerated.

PS-TuP-6 Dry Etching of Co Thin Films Using High Density Plasma of Organic Gases*, **Seon Jae Kim**, E. Lim, S. Park, S. Kim, C. Chung,* Inha University, Republic of Korea

Copper interconnect, which has low resistivity, high electromigration resistance, and good mechanical properties, has replaced aluminum interconnect as the semiconductor devices are scaled down.However, as the semiconductor devices are increasingly scaled down, the metal interconnect line widths have been reduced to a level lower than 39 nm, which is the electron mean free path in the bulk state of copper. The scaling down in interconnect dimensions causes a resistivity size effect in which the resistivity of copper increases rapidly.Meanwhile, cobalt is a promising alternative for next-generation interconnect materials due to its lower resistivity at smaller dimensions (~10 nm), high melting point, and high compatibility with CMOS [1].

Despite the good properties of cobalt, dry etching of Co thin films have not been developed because Co has very low reactivity and its etch byproducts are nonvolatile. Therefore, it is necessary to develop an optimal etching gas and dry etching process for cobalt thin films.

In this study, dry etching of Co thin films patterned with TiN hard mask was carried out using inductively coupled plasma of organic gases. The etch rate, etch selectivity to hard mask, and the etch profile will be investigated using scanning electron microscopy and energy dispersive X-ray spectroscopy. The etch mechanism of cobalt thin films using organic gases will be examined using X-ray photoelectron spectroscopy.

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PS-TuP-8 Selective Etching of Silicon Nitride with Remote ClF_3/H_2 Plasma*, **Seongjae Yu**, K. Kim, Y. Ji, J. Kang, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Highly selective etching of silicon nitride (SiN_x) over silicon oxide (SiO_y) is of great importance for oxide/nitride stacks in a 3D-NAND fabrication process. In this study, selective isotropic etching of SiN_x to SiO_y has been researched by adjusting a ClF_3/H_2 remote plasma in an inductively coupled plasma system. The etch rate of SiN_x over 80 nm/min and Selectivity (SiN_x over SiO_y) of ~130 was experimentally produced using ClF_3 remote plasma at a room temperature. Moreover, when H_2 was added to ClF_3, the selectivity increased to 200 while lowering the etch rate of both SiN_x and SiO_y as F radical is decreased in the plasma. The possible etch mechanism of SiN_x under Cl, F, H radicals was suggested based on the plasma and surface analyses. The etch characteristics of SiN_x and SiO_y according to the substrate temperature showed a higher activation energy of SiO_y compared with SiN_x under ClF_3 plasma.

PS-TuP-10 Layer-by-Layer Etching of Copper Thin Films Under Acetylacetone/O_2 Gas Mixture*, Seung Hyun Kim**, E. Lim, S. Park, C. Chung,* Inha University, Republic of Korea

Previously, acetylacetone (acac) was employed at the gas cluster ion beam etching for copper films. They reported that the etch depth of copper using acac and O_2 gas mixture was deeper than that of copper using O_2 gas only, introducing the possibility of etching for copper films. However, they presented no etch profiles on copper films [1].

In this study, layer-by-layer etching of copper thin films was performed using acac/O_2 gas mixture and Ar plasma. Layer-by-layer etching involves two-step procedure, which contains the surface modification by the exposure of copper films to acac/O_2 gas and the elimination of the modified layers by the sputtering of Ar ions. The surface modification step was optimized by varying the flow-rate ratio of acac/O_2 gases and exposure time, which led to the oxidation of copper films and the formation of copper compounds. In addition, the elimination step also was developed by changing the dc-bias voltage to the substrate and sputtering time. The surface modification and elimination of the modified layers were verified by X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy. The etch per cycle was obtained in the range of 0.7-3.0 nm/cycle, relying on the Ar sputtering at the fixed exposure condition. Layer-by-layer etching of copper films masked with SiO_2 presented good etch profiles without redepositions. Layer-by-layer etching of copper films using acac/O_2 gas mixtures can be one choice to demonstrate the fine pattern on copper films.

AcknowledgementThis work was also supported by Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (P0008458, HRD Program for Industrial Innovation) and This work was also supported by the MOTIE (Ministry of Trade, Industry & Energy (20019504)).

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PS-TuP-11 Enhancement of Plasma Uniformity Controlling Thermal Conductivity by Insulator Ring*, Jinuk Park**, J. Park,* Sungkyunkwan University (SKKU), Republic of Korea

Regardless of the change over time, efforts to keep wafer edge's etch rate (ER) constant became an important area in etching technology as the size of wafer increased and the structure of the chip became more complicated. Therefore, semiconductor manufacturing facilities have developed to precisely etch the edge area. In this study, we developed a thermal interfacial material (TIM) with high thermal conductivity and changed the handling method of the TIM efficiently to improve used TIM Pad thermal conductivity.

TIM is implemented in the form of a pad having a heat dissipation component by adding thermal conductive fillers (AlN, Al2O3, Al) to a silicon-based resin. In this study, we will show you that feature of TIM pad depending on how to make TIM pad.

The characteristics of TIM pad is changed depend on how to deal with pad. In this paper, we will studied changed characteristic of TIM pad how long pad exposure to atmosphere and when does it make.

PS-TuP-12 Effect of $C_4H_2F_6$ Isomers on the Etch Characteristics of SiO_2*, Hyejoo Lee**, H. Tak, S. Kim, D. Sung, T. Park, J. Kim, J. Min,* Sungkyunkwan University (SKKU), Republic of Korea*; W. Long,* Sungkyunkwan University (SKKU), China*; D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

As the device structure is scaling down in semiconductor devices, the requirements of higher selective etching process are increased. To meet the requirements, high aspect ratio contact (HARC) etching process is being developed in the direction to use more polymer forming fluorocarbon (PFC) and hydrofluorocarbon (HFC) gases. In addition, the PFC/HFC gases used for HARC etching for DRAM and 3D NAND devices such as C_4F_8, CHF_3 etc. have a long lifetime in the atmosphere when exhausted and have a high global warming potential (GWP) simultaneously. Therefore, to improve the etch selectivity for HARC etch processes and to replace the high GWP gases with low GWP HFC/PFC gases, various HFC/PFC gases are under investigation.

In this study, to understand the effect of the molecular structure of HFC gases on the etch characteristics of SiO_2 and its relationship to the GWP, $C_4H_2F_6$ isomer gases which are one kind of the high polymer forming HFC gases were used, and their dielectric etch characteristics and global warming effect depending on their molecular structure were investigated. Even though the chemistry of the HFC isomers is the same, due to the different molecular structures, in addition to differences in the boiling points and the global warming potentials, the etch characteristics were different especially at a critical oxygen mixing percentage due to the differences in gas dissociation related to the specific chemical structure of $C_4H_2F_6$ isomer.

PS-TuP-13 Analysis on Ion Energy Distribution and Ion Mean Energy for All Radio-Frequencies and Pressures*, Inho Seong**, S. Kim, Y. Lee, C. Cho, W. Jeong, Y. You, S. You,* Chungnam National University, Republic of Korea

As low-temperature plasmas have played a crucial role in modern semiconductor manufacturing, the understanding of ion energy distribution (IED) and ion mean energy at the electrode according to external control parameters is essential for satisfying a design rule. We studied IEDs and ion mean energy at the electrode in a wide range of frequency and pressure with an ion trajectory simulation coupled to Monte Carlo collision method. We observed a new tendency for the ion mean energy to increase and then decrease from low to high frequency in low pressure so that we analyzed ion trajectories for frequency and pressure regime. In addition, we found the frequency trend of the ion mean energy including the frequency region in which the ion mean energy is unchanged at a relatively high pressure and the frequency region shift of maximum ion mean energy. We are expected that these results show a different interpretation of the collision known as reducing the ion energy in the sheath.

PS-TuP-14 Moving Toward Antibacterial Wound Dressings: Modifying Commercially-available Materials Using Pulsed and Continuous-wave 1,8-cineole Plasma*, Mia-Rose Kayaian**, M. Hawker,* California State University, Fresno

Hospital-acquired infections (HAIs) are one of the primary causes of mortality. According to Medicare data, HAIs are estimated to cost the United States anywhere from 28.1 to 96.8 billion dollars yearly. Most HAIs begin with bacterial attachment to the wound and, if left untreated, the infection site can become a chronic wound. For existing chronic wounds, oral and topical antibiotics are the clinical standards. This can become problematic because of the potential development of antibiotic resistance. Thus, incorporating a modification to the wound dressing that actively kills bacteria on contact without creating antibiotic resistance would be the best outcome for treating chronic wound infections. Plasma-enhanced chemical vapor deposition (PECVD) using 1,8-cineole (an active component of eucalyptus oil) as the plasma feed gas has been shown to actively kill bacteria on the surface of glass slides. Yet, 1,8-cineole-based PECVD strategies have not been extended to wound dressing materials.

The goal of the present study was to use 1,8-cineole PECVD to modify commercially-available wound dressing materials. By adjusting PECVD parameters, such as changing the applied power, it is possible to control the coating chemistry. However, no attempt has been made to compare pulsing vs. continuous-wave deposition. In other PECVD systems, pulsing has enabled the plasma precursor functional groups to be maintained within the coating. Because the functional groups give 1,8-cineole its antibacterial properties, we anticipated pulsing would enable the functional groups to be maintained upon PECVD. We hypothesized that wound dressing materials treated using pulsed plasma conditions would exhibit greater antibacterial properties compared to those treated with continuous conditions because pulsing allows for the functional groups to be maintained. Water contact angle goniometry was used to evaluate changes in surface wettability before and after plasma treatment. Additionally, x-ray photoelectron spectroscopy was used to quantify the elemental composition of plasma-treated and control surfaces. Zone of inhibition testing was performed to evaluate antibacterial properties against both gram-positive and gram-negative bacteria. Overall, previously established 1,8-cineole PECVD strategies were extended to wound dressing materials. This work represents progress towards addressing the need to directly target chronic wound infectious sites.

PS-TuP-15 To What Extent Do Nitrogen and Water Vapor Plasma Treated Silk Films Exhibit Hydrophobic Recovery?*, Ashley Keobounnam**, C. Lenert-Mondou, M. Hawker,* California State University, Fresno

Silk fibroin (silk) is a naturally-derived polymer from the bombyx mori cocoon. Silk has great potential applications for biomedical use due to its mechanical strength, non-immunogenic properties, and ability to biodegrade. However, the hydrophobic nature of silk can cause challenges with cell adhesion in vivo. Therefore, modification must be performed to improve the surface hydrophilicity. Low-temperature plasma (LTP) modification is a well-established method for polymer modification and has the benefits of being a solvent-free process. Nitrogen and water vapor LTP are both well-documented as strategies to enhance polar functional groups on a polymer's surface. However, LTP-modified polymers have been documented to experience hydrophobic recovery. During hydrophobic recovery, the modified polymer chains rearrange from a higher to lower surface energy state, negating the effects of LTP modification. Notably, the hydrophobic recovery of LTP-modified silk has not been previously studied.

The goal of this study was to systematically evaluate the hydrophobic recovery of nitrogen and water vapor LTP treated silk films. Silk films were dropcast on glass slides and were LTP-modified using optimized plasma parameters (applied power, pressure, and treatment time). Interactions between silk films and water were evaluated with water contact angle goniometry. Initial results showed that untreated silk films exhibited water contact angles of 69 +/- 1°. After nitrogen and water vapor LTP treatments, the films showed water contact angles of 35 +/- 1° and 25 +/- 2°, respectively, demonstrating a significant decrease in hydrophobicity. Films were then aged under ambient conditions up to 6 weeks and analyzed at specific time points (0 days, 7 days, 21 days, and 42 days). Both the nitrogen and water vapor plasma-modifed silk film water contact angles remained relatively stable throughout the 42 day aging period, suggesting that minimal hydrophobic recovery occurred.

PS-TuP-16 Ion Energy Control Independent with Ion Density Using a Passive Antenna in an Inductively Coupled Plasma Source*, **Minsu Choi**, S. Kim, I. Seong, C. Cho, Y. Lee, W. Jeong, Y. You, B. Choi, S. You,* Chungnam National University, Republic of Korea

As elaborate etching such as atomic layer etching becomes a challenge in modern semiconductor and display processes, The precise independent control of ion energy and density for accurate etching has attracted tremendous interest. While previous techniques have focused on a variant of the electrical system called active control, this study proposes a method via a passive antenna without active control.

The proposed technique controls electromotive force induced by the inductive coupling between the discharge antenna and the passive antenna, which varies plasma potential and finally ion energy. To verify the proposed technique, ion energy distribution (IED) and plasma potential were measured by an ion energy analyzer and emissive probe, respectively, and the electromotive force was controlled by adjusting the distance between those antennae.

The experiment result shows the increase of plasma potential and ion energy with constant ion density as the antennae distance decreases. This result means that ion energy can be controlled independently of ion density by using the passive antenna.

This study demonstrated the ion energy control technique independent of its density with a passive control and would be applicable for future semiconductor processing.

PS-TuP-17 The Impact of Si_3N_4 Ultra-thin Layer on InN Growth on Si(111) by RF-MOMBE*, **Wei-Chun Chen**,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan*; S. Chen, C. Cheng,* Department of Mechatronic Engineering, National Taiwan Normal University, Taiwan

Si_3N_4 ultra-thin layer were grown on Si(111) surface by RF N_2 plasma exposing with various N_2 flow rate and nitriding time. After the Si_3N_4 thin films were as a buffer layer for the InN crystals growth. We discussed the effect of InN/Si_3N_4 ultra-thin film on the optical, chemical, structural properties. The results indicated that stoichiometric Si3N4 ultra-thin film was obtained at nitridation time nearly to 1hr with RF power of 300 W and N2 flow ratio at 1.2 sccm. Also, AFM image exhibited that the Ra roughness of Si_3N_4 is 0.39 nm. On the other hand, XRD phi-scan results shows that the InN crystals epitaxy growth with Si(111) substrate. Also, the InN crystals were detected single crystals growth with grown the crystal along the <0001> direction (c-axis). Cross-sectional SEM images show the nanocolumns with surface texturing of pyramid-like.

PS-TuP-18 Machine Learning Based Surrogate Models for Capacitively Coupled Plasmas*, L. Yan,* Applied Materials, Inc. (Currently with University of Pennsylvania)*; **Abhishek Verma**, S. Ganta, K. Bera,* Applied Materials, Inc.

Plasma simulations are instrumental in understanding fundamental plasma behavior in plasma reactors used for etching and deposition processes in semiconductor manufacturing. However, these models are often slow to execute for large scale problems, limiting their applicability in design optimization and process control. To overcome these limitations, we recently developed a machine learning framework based on deep learning methods (LSTM and CNN-AE) to construct surrogate models at reduced computational cost while maintaining accuracy. Radio frequency (RF) plasma simulations have been performed using in-house code for Ar discharge. RF potential amplitude and phase differences at several harmonics are generated utilizing design of experiments and used to drive the plasma at different pressures. We used plasma characteristics from simulations, such as generated current $I(t)$, plasma density $n(x,t)$ with respect of voltage $V(t)$ to train and test on datasets under different conditions (e.g., pressure). We obtained the optimal model through experiments with comprehensive search of different hyper-parameters and model architectures. In time series prediction of current $I(t)$, we used n past values of two voltage channels and their time derivatives as inputs to a LSTM based model and showed that averaging prediction results given by models trained on different past values could lead to further accurate and smooth results. Furthermore, our model performs satisfactorily for the prediction of current $I(t)$ even at a different operating frequency from the one that the model was trained on. Finally, we demonstrate optimal compression of spatial variables such as plasma density $n(x,t)$ using CNN based autoencoder.

PS-TuP-19 Chemistry Reduction in Fluid Plasma Simulations*, **Ramanish Singh**,* Applied Materials Inc. (Currently with University of Minnesota)*; S. Ganta, A. Verma, K. Bera,* Applied Materials, Inc.

Plasma modeling for semiconductor process applications can help in gaining insights into various mechanisms occurring during the processes, playing a vital role in optimizing these processes. However, as the complexity of the plasma chemistry increases (large number of species and reactions), these models become prohibitively expensive in terms of computational cost. Such chemistries can be reduced by removing unimportant species and reactions to reduce computational cost with minimal loss in accuracy. To this end, we developed a general Python-based chemistry reduction methodology that utilizes fluid plasma simulation results for identifying important chemical pathways based on production rates of relevant species thereby generating multiple sets of reduced chemistries. We use PumpKin[1], an open-source C++-based software for identifying important chemical reaction pathways given a chemistry with reaction rates and stoichiometric data from a plasma simulation. Once the multiple reduced chemistries are obtained, the chemistry reduction model assesses their accuracy, helping with the selection of the most suitable reduced chemistry for a particular application. We also developed an alternate technique for chemistry reduction involving direct species removal, wherein species and their associated reactions are removed based on their steady-state time-averaged densities relative to that of other similar species in the chemistry. We tested the two methodologies for chemistries belonging to different plasma processes such as plasma-enhanced chemical vapor deposition (PECVD), plasma-enhanced atomic layer deposition (PEALD), and conductor etch. We observe that chemistry reduction model based on species production rates removes a high number of unwanted reactions (~40-50%) and around 5-6 % of unimportant species while maintaining an error of less than 3% between the full chemistry and the reduced chemistry. In the direct species removal algorithm, although the number of species removed is marginally higher for a given error threshold, very few reactions get eliminated. We also investigated the effect of running both the algorithms in the two possible two-step sequences. The model based on species production rates followed by direct species removal results in a chemistry reduction with a good balance between model accuracy and computational cost optimization. However, the results can vary according to the chemistry used in the semiconductor process application.

1. Markosyan, Aram H., et al. "PumpKin: A tool to find principal pathways in plasma chemical models." *Comput. Phys. Commun.* 185.10 (2014): 2697-2702.

Applied Surface Science Division
Room 320 - Session AS+BI+CA+HC+LS+PS+SE+SS-WeM

Analysis of Surfaces and Interfaces Related to Energy and the Environment

Moderators: Kateryna Artyushkova, Physical Electronics, **Tony Ohlhausen**, Sandia National Laboratory

8:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-1 Adhesion Properties of Industrial Steel Samples***, **Lukas Kalchgruber**, M. Hahn, L. Mears, M. Valtiner,* TU Wien, Austria

Solving industrial questions is of utmost importance to improve material properties, developing industrial applications and understanding fundamental processes. One of these questions is how different pre-treatments alter the adhesion process between steel and polymers.

To study the effect of the pre-treatment on the subsequent adhesion process, steel was treated either thermally or via plasma.

To characterize adhesion, the surface force apparatus (= SFA) was utilized in reflection mode. In the SFA experiment, the steel is brought into contact with another surface which is prepared on a fused silica optical disc. Before the optical discs can be used in SFA, a semitransparent, reflective layer needs to be deposited on the curved surface. Additionally, they were spin coated with few µm thin, homogeneous, smooth layers of SEBS polymer. Afterwards, a suitable particle free contact was established between the polymer and the steel sample in the SFA, which generated the following data types:

1. Newton rings à Provide information about the contact area
2. Force data à Adhesive pressure (referenced to contact area)
3. Fringes of chromatic order (= FECO) à Time-Distance-Curves

The main selling points of this technique are as follows: firstly, the model system is very close to the actual problem, as the steel sample in question can be used directly. Secondly, direct information about the adhesive pressure can be obtained. Thirdly, considerably more information about the adhesive behavior of the system is available beyond just one number.

The SFA results achieved are promising. We have a method that allows us to quantify the adhesive pressure in a model system and differentiate between differently treated steel samples. We have further put our adhesion results into context with the support of XPS characterization of the surface. Thermally treated samples have a hydroxide/oxide ratio of roughly 50/50 while samples treated with plasma show a ratio of 90/10. The hydroxide to oxide ratio correlates with the adhesion measured by SFA, which emphasizes the role of hydroxide in preventing adhesion.

8:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-2 An Electrochemically Polymerized Protective Layer for Magnesium Metal Anode***, Y. Wang,* University of Maryland College Park*; **Alexander Kozen,*** University of Maryland

Rechargeable magnesium (Mg) batteries are promising beyond Li-ion technologies due to their high volumetric capacity (3832 mAh cm^{-3}) and high natural abundance. Nonetheless, Mg metal anode is incompatible with most conventional electrolytes which leads to the formation of an ionically passivating layer. Mg also suffers from growth of dendrites similar to Li, which causes failure of the cells. In this study, we electrochemically polymerized 1,3-dioxolane (DOL) to form a thin Mg^{2+}-conducting elastomeric artificial solid electrolyte interphase (ASEI) layer by electrochemically pretreating Mg metal anodes. We found that this protective ASEI layer enables excellent cyclability of Mg-Mg symmetric cells at high current density (0.5 $mAcm^{-2}$) over 400 hours at a stable low overpotential (0.50 V vs. Mg^{2+}/Mg) without cell short-circuiting, while untreated pristine Mg symmetric cells quickly failed. The formation of this ASEI also significantly lowered the impedance of the cells, which proved its capability of conducting Mg^{2+} ions. Comprehensive surface chemistry analysis was done by X-ray photoelectron spectroscopy (XPS) which showed that an ASEI mainly consists of poly-DOL was formed, along with various Mg salts which are instrumental to the conductance of Mg^{2+} ions. More importantly, poly-DOL component in the elastomer was well preserved post-cycling, which contributed to the long-term cyclability and low voltage hysteresis of pretreated Mg-Mg cells, as compared to the pristine ones. Focused ion beam (FIB) – scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that a generally uniform layer was formed on the surface and this ASEI is roughly 200 µm thick and was able to suppress the growth of Mg dendrites after cycling for 400 hours at 0.03 mA cm^{-2} current density, as compared to the rampant sphere-shaped dendrites on the surface of pristine Mg anodes after cycling. This is the first ever report on the successful formation of poly-DOL ASEI on Mg metal anodes as a protective layer and by electrochemical polymerization method that effectively enhanced the electrochemical cycling performance of the Mg metal anodes.

8:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-3 Analysis of Surfaces and Interfaces in Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Devices***, **Svitlana Pylypenko**,* Colorado School of Mines **INVITED**

Implementing a hydrogen-based infrastructure depends on developing electrochemical energy conversion devices such as fuel cells and electrolyzers. Polymer electrolyte membrane fuel cells (PEMFCs) have been the focus of research for lightweight renewable transportation applications such as motor vehicles for years, but they also offer the potential to fuel stationary applications, including residential power, due to their potential to produce industrial amounts of energy via a renewable route. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy to produce and store renewable energy in the form of hydrogen for subsequent use in either manufacturing processes, or to run a fuel cell, which can generate electricity on demand.

Great improvements have been made in the development of catalysts and electrodes for PEM systems, improving their activity and stability while reducing the amount of precious metals used. The properties of the electrodes used in these devices are influenced by multiple parameters: the chemical identity of the catalyst and the ionomer; the morphological properties of the catalyst (e.g. shape and surface area); ink formulations; and the various processing parameters used to prepare the electrode. Due to the breadth of possible variable combinations and the inherent complexity of electrode materials, it is unsurprising that PEM electrodes are both morphologically and chemically heterogeneous. Characterization of relevant surfaces and interfaces in these devices, therefore, represents a challenge that requires a multi-technique approach that evaluates all relevant scales and properties and brings a better understanding of the evolution of surfaces and interfaces under more realistic conditions. This talk will discuss the progress towards the comprehensive characterization of the most critical surfaces and interfaces in PEM devices using a combination of X-ray and electron spectroscopy and microscopy methods. Several challenges related to the characterization of catalyst-gas and catalyst-ionomer interactions in these systems will be covered along with results obtained with near-ambient pressure x-ray photoelectron spectroscopy (nAP-XPS). The development of characterization strategies to enable the exploration of a large processing parameter space will be presented, which can then be used to fabricate optimized electrodes with state-of-the-art catalysts as well as electrodes that integrate novel catalysts, all made with scalable routes. And finally, the development of novel approaches toward the characterization of other components of PEM devices such as porous transport layers will also be briefly discussed.

9:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-5 XPS Analysis of Battery Materials***, **Sarah Zaccarine**, B. Schmidt, K. Artyushkova,* Physical Electronics USA*; A. Baniya, Q. Qiao,* Syracuse University

Lithium-ion batteries (LIBs) have experienced success including rechargeability and long lifetimes but their limited energy density restricts applications moving forward. Lithium metal batteries (LMBs) offer similar benefits but with much higher achievable energy densities, making them a promising future battery technology. Both LIBs and LMBs are multi-layered, complex systems with many materials and interfaces that each play a critical role in performance and stability. Tuning the composition and morphology of these materials is necessary to create stable, high-performing devices, but the multi-component interfaces, interactions, and dynamic nature of these systems makes characterization challenging. In order to optimize materials properties and improve battery lifetimes, there is a pressing need for physicochemical characterization approaches with high spatial resolution, chemical and morphological analysis, and correlation of synergistic properties.

X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the chemical composition of battery materials, and the depth resolution (~10nm) is ideal for analyzing thin layers and interfaces. However, modern XPS instruments have a variety of operating modes and analytical accessories that enable characterization across a variety of lateral and vertical size regimes. Small and large spot comparisons can track overall composition and local features and changes, with scanning microprobe analysis allowing for spatial resolution down to a few microns. X-ray induced secondary electron imaging (SXI), including high-resolution mosaic imaging over a wide sample area, can be used for easy identification of important features and morphological imaging of various battery component materials to complement chemical information. Chemical mapping can visualize distribution of individual elements or chemical species to understand how materials are distributed and change with testing. Additional options address stability concerns associated with Li materials, including a cooling stage to preserve battery chemistry during extended experiment times, where time-resolved profiles are used to compare chemical degradation under controlled temperatures, and incorporating Al Kα and Cr Kα X-rays for non-destructive XPS and hard X-ray photoelectron spectroscopy (HAXPES) analysis of surface (up to ~10nm, Al) and subsurface (up to ~30nm, Cr) composition. Combined, these powerful capabilities enable thorough characterization of battery materials properties for micro- and large-area spectroscopic analysis of surfaces and interfaces and how these properties change under various analytical and operating conditions.

9:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-6 Novel Battery Material Analysis with High-Resolution and High-Throughput XPS***, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; C. Moffitt,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Inc., UK*; **Adam Roberts**,* Kratos Analytical Limited, UK

Several material systems will be discussed to give an overview on how XPS can yield information regarding the distribution and chemical speciation of battery materials.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. However, to date, the battery performance has not been competitive, and promising ternary materials have been plagued by poor stability in air and unsatisfactory long-term cycling. Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation [1]

The significance of sensitivity and detection limit, comparisons of surface and bulk and an approach for pragmatic peak fitting of difficult elemental lines will be discussed along with considerations such as etch artefacts and degradation.

[1] Shipeng Jia *et al*., J. Mater. Chem. A, 2022,10, 251-265

11:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-10 Multimodal Analysis and Imaging of the Boehmite Layer on AA6061***, **Lyndi Strange**,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory*; V. Shutthahandan, M. Song, Q. Miller, M. Bowden, J. Gao, Y. Zhang, J. Son, R. Shimskey, R. Prabhakaran,* Pacific Northwest National Lab*; V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10% Mo (U-10Mo) is being considered as a promising alternative to oxide-based dispersion fuel with high-enriched uranium for use in research reactors. The configuration of this proposed LEU monolithic fuel plate consists of the U-10Mo plate-type fuel foil with a 25 µm Zr interlayer barrier clad with an aluminum alloy (AA6061). The clad AA6061 is coated with a boehmite layer to prevent corrosion. The boehmite layer has a high pH passivation range, which makes it resistant to oxidation and preferable to protect the Al cladding. Boehmite is usually formed on the AA6061 surface by autoclave processing. Various surface cleaning techniques have been employed such as polishing and etching to clean the surface of the AA6061 prior to boehmite formation. In this study, we examine how pre-treatment of AA6061 using polishing followed by both acid and alkaline etching affects the chemical composition of the boehmite layer using multimodal analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron microscopy (XPS), transmission electron microscopy (TEM), and grazing incidence x-ray diffraction (GI-XRD) were used to understand the changes in the boehmite layer as a result pre-treatment. ToF-SIMS provides a surface sensitive technique to understand the surface composition and characteristics. Spectral similarities were verified using principal comment analysis (PCA). XPS is a complimentary technique that provides quantitative information about the oxidation states present on the surface. Both the SIMS and XPS results suggested oxidation at the surface, which was further investigated using TEM-SAED and GI-XRD. While the GI-XRD results suggested the dominant phase present on the coupon surface is boehmite, TEM-SAED found small amounts of α- and γ-Al_2O_3 present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov**,* Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects.[1] HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (AMX_3). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.[2-3]

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$(MA = $CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

References:

1. P. K. Nayak, S. Mahesh, H. J. Snaith, D. Cahen, *Nat. Rev. Mater*., **2019**, *4*, 269-285.
2. H. Kaslasi, Y. Feldman, Y. Rakita, D. Cahen, G. Hodes,*Cryst. Growth Des*, **2020**, *20*, 4366-4374.
3. D. R. Ceratti, A. V. Cohen, R. Tenne, Y. Rakita, L. Snarski, N. P. Jasti, L. Cremonesi, R. Cohen, M. Weitman, I. Rosenhek-Goldian, I. Kaplan-Ashiri, T. Bendikov, V. Kalchenko, M. Elbaum, M. A. C. Potenza, L. Kronik, G. Hodes, D. Cahen, *Mater. Horiz.*, **2021**, *8*,1570-1586.

11:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-12 Surface Characterization of Mineral Associated Organic Matters in Environmental Samples by Using X-Ray Photoelectron Spectroscopy (XPS)***, **Qian Zhao**, M. Engelhard, O. Qafoku, K. Hofmockel,* Pacific Northwest National Laboratory

Surface characterization is an important analytical approach to understanding the most dynamic interface of a material. The understanding of soil organic matter (SOM) persistence is critical to global carbon (C) cycling. Minerals play an important role in persisting SOM by associating with organic matters (OM) through different interactions. Yet mechanisms of the accumulation of OM in soil are still unclear. Chemical characterization of OM that is associated with minerals provides a mechanistic understanding of mineral-OM interactions. X-ray photoelectron spectroscopy (XPS) analysis allows us to probe the chemical states and speciation of OM on the surface of mineral grains or soil particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we adsorbed four organic compounds on a calcite crystal. XPS analysis found the relative concentration of C was higher in OM adsorbed calcite than that in pristine calcite. Further, the deconvolution of C 1s spectra reveals that the calcite surface had a relatively lower abundance of carbonate but a higher abundance of alkanes in the OM adsorbed calcite than pristine calcite, indicating the adsorption of OM on the calcite surface. In the soil system, we incubated agricultural soils with ^{13}C-glucose for 12 months to trace the fate of microbial residues. Size and density fractionation was used to separate mineral-associated organic matter (MAOM) from whole soil. XPS analysis determined C chemistry of necromass on soil particle surfaces by scanning C 1s region of MAOM and non-MAOM fractions. We found that the MAOM fraction had a relatively higher abundance of carbonyl and carboxylic C functional groups and a relatively lower abundance of C-C/C=C group than non-MAOM fraction. It suggests that MAOM fraction is enriched in microbial-derived molecules (i.e., proteins) but has fewer plant detritus (i.e., carbohydrates or lignin) on mineral surfaces. XPS technique allows us to understand the surface chemistry of microbial necromass that is associated with minerals in soil. The chemical speciation information provides us with the potential bonding environment at the interface of minerals and OM.

Plasma Science and Technology Division
Room 305 - Session PS1+AP+TF-WeM

Plasma Deposition and ALD Processes for Coatings and Thin Films

Moderators: Sumit Agarwal, Colorado School of Mines, **Adriana Creatore**, Eindhoven University of Technology, Netherlands

8:00am **PS1+AP+TF-WeM-1 Hollow Cathode Enhanced Capacitively Coupled Plasmas in Ar / N_2 / H_2 Mixtures and Implications for Plasma Enhanced ALD**, ***David Boris,*** U.S. Naval Research Laboratory; *M. Johnson,* Syntek Technologies; *C. Eddy,* ONR Global; *S. Walton,* U.S. Naval Research Laboratory

Plasma enhanced atomic layer deposition (PEALD) is a cyclic atomic layer deposition (ALD) process that incorporates plasma-generated species into one of the cycle sub-steps. The addition of plasma is advantageous as it generally provides unique gas-phase chemistries and a substantially reduced growth temperature compared to thermal approaches. However, the inclusion of plasma, coupled with the increasing variety of plasma sources used in PEALD, can make these systems challenging to understand and control. This work focuses on the use of plasma diagnostics to examine the plasma characteristics of a hollow cathode enhanced capacitively coupled (HC-CCP) plasma source, a type of plasma source that has seen increasing attention in recent years for PEALD. Ultraviolet to near-infrared (UV-NIR) spectroscopy as well as spatially resolved Langmuir probe and emissive probe measurements are employed to characterize an HC-CCP plasma source using nitrogen based gas chemistries typical of nitride PEALD processes. Spectroscopy is used to characterize the relative concentrations of important reactive and energetic neutral species generated in HC-CCP systems as a function of applied RF power, gas chemistry and pressure. In addition, the electron energy distribution function, electron temperature, plasma potential, and plasma density for the same process parameters are examined using an RF compensated Langmuir probe and emissive probe.These measurements indicated that electron temperature (T_e), electron density (n_e), and plasma potential (V_p) varied significantly over the operating conditions examined with Te varying from 1.5 to 8 eV, Vp varying from 30V to 90V, and ne varying between 10^{15} m-3 and low 10^{16} m-3.This wide range plasma conditions is mediated by a mode transition from a low T_e, high ne mode of operation at low pressure (<100 mTorr) to a high T_e, low n_e mode at higher pressures (>100 mTorr).These operational modes appear analogous to the classical γ and α modes of traditional capacitively coupled plasmas.Atomic N and H densities also vary significantly over the operating conditions examined.

8:20am **PS1+AP+TF-WeM-2 Chasing Oxygen Out of Nitrides Grown on PEALD and Thermal ALD**, ***Bangzhi Liu,*** The Pennsylvania State University; *B. Rayner,* KJ Lesker

It is not uncommon to see O content above 10% inside nitrides grown on both thermal and plasma ALD reactors. One typical example is TiN. Ti is extremely reactive and will combine with any O present inside the reactor. It has been reported that O can come from multiple sources [1], including o-ring seals, impurities inside UHP gases (Ar and N2), plasma tube, etc. By adding differential pumping to gate valve seal, chamber seal, and plasma tube seal on our Lesker 150LX system, and purifying Ar and N2 gases, the O level is reduced below 1% inside TiN film. By correlating TiN growth per cycle, ellipsometry thickness uniformity mapping, and sheet resistance to O level measured by XPS, we can monitor O level inside the reactor precisely and verify the ultra-high purity (UHP) condition of the chamber. By maintaining UHP condition, extreme high purity AlN and BN have been prepared. Surprisingly, extremely low-level O (barely detectable by XPS) was found inside ZrN prepared on our thermal ALD reactor, Lesker 150LE due to a special design of the chamber. This opens a door to high purity nitrides on thermal ALD reactor. In this talk, experimental data will be presented to show the interaction between O level inside ALD nitrides and system design.Practical engineering controls enabling UHP nitrides will be discussed.

[1] Ultrahigh purity conditions for nitride growth with low oxygen content by plasma enhanced atomic layer deposition, J. Vac. Sci. Technol. A 38, 062408 (2020); Gilbert B. Rayner, Noel O'Toole, Jeffrey Shallenberger, et al.

8:40am **PS1+AP+TF-WeM-3 Area-Selective Deposition: A Bottom-Up Approach to Nanoelectronics Fabrication**, ***Silvia Armini,*** IMEC, Belgium **INVITED**

Area-selective deposition (ASD)-driven processes recently gained a lot of attention from the microelectronics industry as a potential solution for the issues associated with top-down pattern formation at the nanoscale.

The first part of this talk is focused on the ASD of TiO_2 and Ru deposited by atomic layer deposition (ALD). In this respect, as an ALD inhibition route, we have been investigating both hydrogen and halogen plasma surface modification of amorphous carbon materials (non-growth area) and methyl-terminated monomolecular organic films on SiO_2 (non-growth area) substrates. On one side, on a-C non-growth area, we examined the possibility of combining two defect-reduction strategies by employing low power Cl_2 or CF_4 plasmas for both surface functionalization/re-functionalization and for removal of nuclei.

The second part of this talk is focused on selective metal passivation films for Dielectric on Dielectric deposition. We review our current understanding of the relationship between structure and properties of the inhibiting materials and the correspondent surface dependence of different ALD processes. Nucleation and growth behaviour of ALD on different surfaces functionalized by organic films will be analyzed, such as the interaction between ALD conditions (i.e. temperature, coreactants...) and the extent of decomposition and modification of the organic films.

9:20am **PS1+AP+TF-WeM-5 The Role of Plasma in Plasma Enhanced Atomic Layer Epitaxy**, ***Scott Walton,*** *D. Boris,* US Naval Research Laboratory; *M. Johnson,* Syntek Technologies, Inc.; *V. Wheeler, J. Woodward, S. Rosenberg, S. Johnson,* US Naval Research Laboratory; *K. Ludwig,* Boston University; *J. Hite, C. Eddy,* US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PE-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma.This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce films of varying characteristics and has been successfully employed to grow epitaxial films.The plasma-based advantages come at the cost of a complex array of process variables that can drastically impact the resulting film properties.We employ plasma diagnostics to inform the choice of process conditions for PE-ALD systems including VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the plasma used in commercial and research PE-ALD tools.In particular, we assess the total ion flux reaching the substrate surface, spatial variation of plasma properties, and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions typically used to grow epitaxial nitride and oxide films. Changes in plasma parameters are then linked with changes in growth modes and characteristics of films including AlN, InN, TiO_2 and Ga_2O_3. This work is partially supported by the Office of Naval Research and the Naval Research Laboratory base program.

9:40am **PS1+AP+TF-WeM-6 Plasma-Enhanced Atomic Layer Deposition of TiAlN Thin Films: A Novel Approach for MAX-phase Synthesis**, ***Moses Nnaji,*** Georgia Institute of Technology, USA; *D. Hitchcock,* Savannah River National Laboratory, USA; *E. Vogel,* Georgia Institute of Technology, USA

MAX-phases are a class of layered hexagonal carbides and nitrides that possess a hybrid metal-ceramic character with a desirable combination of mechanical properties.[1] Consequently, many MAX-phase coatings are attractive for applications requiring extreme heat and corrosion resistance. However, conventional synthesis of MAX-phases such as $Ti_{n+1}AlX_n$ requires high-temperatures (800-1000 °C), limiting applications for temperature-sensitive materials.[2] Plasma-enhanced atomic layer deposition (PEALD), however, may be capable of MAX-phase $Ti_{n+1}AlX_n$ synthesis at low temperatures (<600 °C) since it (1) uses forms of energy other than high temperature to achieve crystallization and (2) creates short elemental diffusion distances to lower the energy necessary for atomic migration and crystallization. Using gaseous precursors and plasma co-reactants, the layer-by-layer growth mode of PEALD boasts conformal deposition of various carbides and nitrides at low temperatures (150-300 °C).[3] However, PEALD has yet to be demonstrated for synthesis of MAX-phase thin films.

By characterizing the stoichiometry and crystallinity of PEALD-grown films, our work explores the viability of PEALD for synthesis of MAX-phase Ti_2AlN. In this work, tetrakis(dimethylamido)titanium (TDMAT) and trimethylaluminum (TMA) precursors with N_2/H_2 plasmas are used for deposition of composite TiAlN films on SiO_2/Si and Al_2O_3 substrates, which are then annealed under various conditions. Our work shows that the Ti:Al ratio can be easily controlled by the TDMAT:TMA cycle ratio, while higher growth temperatures and H_2 plasma induce N-deficient TiN and Al layers for a stoichiometry closer to the composition of Ti_2AlN. Furthermore, annealing of PEALD-grown TiAlN is observed to induce desorption of Al and N, a mechanism seen in conventionally sputtered Ti/AlN composites that leads to formation of MAX-phase Ti_2AlN. The effects of contamination and as-deposited crystallinity on the final composition and structure of annealed PEALD-grown TiAlN are investigated.

[1]Barsoum, M. W. et al. (2000). *Prog. Solid. State Chem.*, *28*(1-4), 201-281.

[2]Eklund, P. et al. (2010). *Thin Solid Films*, *518*(8), 1851-1878.

[3]Profijt, H. B. et al. (2011). *J. Vac. Sci. Technol. A: Vac. Surf. Films*, *29*(5), 050801.

Acknowledgments: This work was supported by Battelle Savannah River Alliance, LLC under Contract No. 89303321CEM000080 with the U.S. Department of Energy and performed in part at the Georgia Tech Institute for Electronics and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542174).

11:00am **PS1+AP+TF-WeM-10 AVS Graduate Research Awardee Talk: Temporal Evolution of Densities and Temperatures in Sub-Microsecond Pulsed Microwave Discharges***, **Dhruval Patel**[1,2], T. Choi, H. Swearingen,* University of Illinois at Urbana Champaign*; D. Jacobson,* Lyten*; J. Bruehl,* University of Illinois at Urbana Champaign*; B. Gittleman, M. Stowell,* Lyten*; E. Barlaz, S. Dubowsky, D. Ruzic,* University of Illinois at Urbana Champaign

Material synthesis in plasma reactors have been long investigated as an alternative to more traditional thermochemical reactors. The promise of efficient reaction channels has extended the use of plasmas in synthesis of more exotic materials such as graphene. Ever since its discovery, tremendous effort has been put towards realizing a scalable plasma-based graphene synthesis process. However, further optimization of these reactors is still required before a commercially viable process can be achieved.

Non-thermal pulsed plasma discharges can provide a gateway to a more efficient conversion of methane, primarily due to enhancement of vibrational excitations. In such discharges, the electron, vibrational and rotational temperatures can vary over the duration of the pulse and must be accounted for to accurately describe the reaction kinetics. This work aims to obtain these temperatures along with densities of hydrogen in the methane discharge over the course of the pulses to both characterize the plasma and estimate methane cracking efficiency. We also consider the hydrogen radical density as this can be used as a proxy to understand the reactions mechanisms. To do so, time gated emission spectrums for the Ar-CH_4 plasmas are obtained and analyzed. The electron temperature is inferred from various $Ar2p_{10-1}$ – $Ar1s_{5,2}$ transitions spanning 690 nm - 815 nm. The vibrational and the rotational lines are determined by spectral fitting of C_2 swan bands or CH A^2D-^2C bands. Hydrogen densities are obtained using actinometry by using trace amounts of Kr (<0.5%). A simple model is used to deduce the approximate densities of hydrogen radicals by comparing the emission of H_b to Kr $3p_{9,8,6}$ (431.96 nm, 431.86 nm, and 427.4 nm) and H_a to Kr $2p_{3,2}$ (557.03nm and 587.09 nm). Combined, these measurements will provide valuable insight into the characteristics and breakdown efficiency of methane containing pulsed plasmas.

11:20am **PS1+AP+TF-WeM-11 In situ Atomic Layer Doping Coupled Low-temperature Epitaxial Growth of β-Ga_2O_3 Films via Plasma-enhanced ALD***, **Saidjafarzoda Ilhom**, A. Mohammad, J. Grasso,* University of Connecticut*; A. Okyay,* Stanford University*; B. Willis, N. Biyikli,* University of Connecticut

Wide bandgap (WBG) semiconductors, such as GaN and SiC make up the key components of high-power high-frequency electronic devices, such as, smart power grids, 5th generation (5G) technology, and electric transportation systems. However, production complexity and high cost of these materials make such technologies less available. Gallium oxide (Ga_2O_3) is an emerging ultra-WBG semiconductor attracting great attention due to its superior electrical properties (larger bandgap ~4.9 eV, high dielectric constant 6-8 MV/cm). Additionally, to compete against the mature WBG materials which are grown typically at 700 – 1000 °C, a substantially lower temperature deposition technique for crystalline Ga_2O_3 is of particular importance for its integration with temperature-sensitive substrates or device structures.

In this study, we report on the low-temperature deposition of crystalline Ga_2O_3 films on Si, sapphire, and glass substrates via hollow-cathode plasma-assisted ALD. Films were grown using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed at 240 °C substrate temperature and 50 W rf-power. Additionally, each unit AB-type ALD-cycle was followed by an *in situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Furthermore, we have employed *in situ* atomic layer doping to n-type dope *β*-Ga_2O_3 films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Both *in situ* and *ex situ* ellipsometry were employed to measure the thickness and optical properties of the films. The samples exhibited enhanced growth-per-cycle (GPC) values around 1.3 Å. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga_2O_3 film signature with monoclinic *β*-phase. High-resolution transmission electron microscopy (HR-TEM) revealed the epitaxial relationship of the Ga_2O_3 layers grown on sapphire substrates. Further results from our ongoing structural and electrical characterizations will provide additional insight to overcome the challenges in achieving device quality undoped and doped *β*-Ga_2O_3 layers at low growth temperatures. Comparison of Si and Sn-doping strategies will be discussed, and if needed, ex-situ thermal annealing studies will be carried out for doping activation.

11:40am **PS1+AP+TF-WeM-12 Plasma-Polymer Coating of Li-Metal Anodes for the Improvement of Li-Ion Batteries***, **Yannik Moryson**, H. Hartmann, S. Otto,* Justus Liebig University Giessen, Germany*; X. Fang,* Technical University of Darmstadt, Germany*; M. Rohnke, J. Janek,* Justus Liebig University Giessen, Germany

The demand for batteries with higher energy densities for electro mobility and energy storage still raises the question for a working lithium metal anode in battery systems. The native passivation layer on top of Li-foils is not suited to enable stable cycling of corresponding electrochemical cells due to inhomogeneities and impurities in the layer composition. These inhomogeneities and impurities will result in locally varying current densities, which lead to dendrite growth and ultimately cell failure. Artificial protection layers are one promising option to overcome these drawbacks and enable the use of lithium anodes. Here, plasma polymer coatings are a quite promising approach.

In this study, we used a self-constructed inductively coupled radio frequency (rf) plasma reactor to clean Li-foils in a first step and after that performed plasma polymerization of 1.4 bis(trifluoromethyl)benzene to deposit a passivation layer on top of lithium metal anodes and characterized the layer with time-of-flight secondary ion mass spectrometry, x-ray photoelectron spectroscopy and scanning electron microscopy. The mechanical properties of the layer were examined by nanoindentation. The results were compared with a commercial Parylene HT polymer to verify the plasma polymerization process. Additionally, we performed $^{18}O_2$ isotopic exchange experiments to determine the diffusion coefficients of oxygen in untreated Li-foils at room temperature $D = 6.3 \pm 0.5\cdot10^{-20}$ cm^2/s and for oxygen in the plasma polymer at room temperature $D = 3.0 \pm 0.2\cdot10^{-23}$ cm^2/s, which showed the protective nature of the coating. Symmetric cell tests with the coated Li electrodes showed a stable cycling behavior for over 300 h with overpotentials below 0.1 V. The electrochemical performance was clearly improved in contrast to cells with uncoated Li.

12:00pm **PS1+AP+TF-WeM-13 Fabrication and Evaluation of Composite Thin Film Membranes for Tritium Management in Future Fusion Plants***, **Adam Job**, C. Li,* Colorado School of Mines*; T. Fuerst, C. Taylor,* Idaho National Laboratory*; J. Way, C. Wolden,* Colorado School of Mines

The hydrogen isotopes tritium and deuterium are leading fuels for use in future fusion reactors. While deuterium is relatively abundant and can distilled from seawater, tritium is a radioactive compound with a short half-life that must be continuously generated and recovered from lithium-based breeder blankets. Vanadium (V)-based membranes are a promising candidate for tritium recovery due its high hydrogen permeability, thermal

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

[2] **AVS Graduate Research Awardee**

stability, and neutron tolerance. However, they require application of a catalytic layer to efficiently dissociate/recombine hydrogen and maintain a clean surface. Platinum group metals (Pt, Pd) are effective catalysts but rapidly alloy with V and lose activity. We are developing nanoscale hydrogen-permeable intermetallic diffusion barriers deposited by techniques such as reactive sputtering and atomic layer deposition. In this presentation we describe the plasma cleaning and preparation of these foils as well as the deposition of ceramic nitrides and oxides barrier layers and catalysts layers. We developed a composite structure to efficiently evaluate the hydrogen permeability of these thin films, whose properties can be orders of magnitude different than their bulk counterparts. The performance and stability of these V-based nanocomposite hydrogen membranes was evaluated as a function of temperature and hydrogen pressure. The differences between successful and unsuccessful membranes is assessed and understood through the use of materials characterization including X-ray diffraction and compositional depth profiling using TOF-SIMS and Auger spectroscopy.

Plasma Science and Technology Division
Room 315 - Session PS2+TF-WeM

Plasma Processes of Non-Silicon Related Semiconductors for Energy-Efficient Devices in Power, Photovoltaics and Optoelectronics Applications

Moderators: Kenji Ishikawa, Nagoya University, Japan, **Steven Vitale**, MIT Lincoln Laboratory

8:00am **PS2+TF-WeM-1 Low-Damage Etching of Nitride Semiconductors Utilizing Photo-Electrochemical Reactions***, **Taketomo Sato,*** Hokkaido University, Japan **INVITED**

Gallium nitride (GaN), which is a III-nitride semiconductor, has wide direct bandgap (3.4 eV), high breakdown electric field (3.3x10^{6} V/cm) and high saturation electron velocity (2.7 x10^{7} cm/sec). On the basis of excellent optical and electrical properties, significant progress has been achieved in the GaN and III-nitride based devices, such as ultraviolet laser diodes, white light-emitting diodes, and high-frequency power transistors.

For the fabrication of GaN-based devices, the etching process is one of the key-issues because GaN is a robust material with strong chemical bonds between nitrogen and Ga showing high chemical stability. Among the various etching technique, the photoelectrochemical (PEC) etching method has a great advantage in low damage and high controllability on nitride semiconductors. The PEC etching process consists of anodic oxidation of the surface and subsequent dissolution of the oxide with a chemical treatment. Since the photo-carriers generated near the sample surface is utilized to enhance the oxidation, the etching reactions easily occur even in highly-stable nitride semiconductors. In addition to this, the electrochemical reactions proceed at room temperature and follows Faraday's law. These features allow etching of nitride semiconductors with low damage and high controllability.

In this presentation, I introduce our recent work on the PEC etching of nitride semiconductors for high-power and high-frequency device application. As an example, the PEC etching process has been optimized for recess etching of AlGaN/GaN high electron mobility transistors (HEMTs), a key device in next-generation communication systems. The etching features were drastically changed with both the light wavelength and its irradiation power. Under the optimal condition, we obtained a very slow etching-rate of 0.12 nm/min, leading to a smooth and flat surface with rms-roughness of 0.4 nm. The threshold voltage (V_{th}) of recessed-gate AlGaN/GaN HEMT was precisely controlled by the residual AlGaN thickness after the PEC etching. These features are promising to realize the high-performance HEMTs with a normally-off operation.

8:40am **PS2+TF-WeM-3 Gan Profile Understanding During the Plasma Etching of an HEMT Recessed-Gate with a Photoresist Mask***, **Simon Ruel**,* CEA-LETI, France*; P. Thoueille,* Lam Research Corporation, France*; P. Pimenta-Barros, N. Posseme,* CEA-LETI, France

GaN-based high electron-mobility transistors (HEMTs) constitute the next generation of high power devices after their silicon-based counterparts, because of their higher super-conducting properties offered by a two-dimensional electron gas (2DEG) channel created at the AlGaN/GaN heterojunction. For safety and consumption considerations, a Normally-Off operating mode is desirable, and possible by patterning the transistor gate with a full recess beneath the 2DEG in order to cut physically the conduction. To maximize the final device efficiency, the gate profile as well as the Plasma Induced Damage (PID) need to be well controlled. Therefore, it seems very important to understand the plasma interactions with the GaN and the associated mechanisms responsible for the GaN profile in order to better control it.

In this paper, we propose a morphological study of the gate plasma etching. The study is firstly composed of different tests and characterizations in order to understand and identify the mechanism responsible for the GaN profile. Then, the knowledge was applied to optimize the Process of Reference (POR) towards a more vertical and uniform profile.

After having opening Barc and dielectric layers, the AlGaN/GaN partial recess is done with a Cl_2/BCl_3-based RIE plasma with a photoresist mask. An etching film of the latter step was performed to identify the gate profile formation and eventual defects. We obtained a tapered profile (~50°) due to a polymer deposition on sidewall, growing with the etching time.

The characterization of these products was performed thanks to TEM EDX. The polymer may be mainly composed of C and Cl, with some traces of Ga. The presence of metallic traces explained the non-removal of the layer by an O_2 plasma.

A parametric study allows us to identify the key parameters responsible for the passivation regime and the slope control: the ElectroStatic Chuck Temperature (ESC T°), the amount of BCl_3 in the plasma, and the DC Bias voltage. Coupled with the previous analysis, we can propose a mechanism responsible for the sidewall passivation. Three main contributors are identified: a [C-Cl] compounds redeposition coming from the resist mask erosion, non-volatile Ga-based compounds [Ga-Cl] coming from the etched GaN trench, and a B_xCl_y contribution coming from the BCl_3 dissociation in the plasma.

Finally, we compared the best process obtained to the POR : it shows a more vertical and uniform GaN profile (80°) against a tapered profile with a double-slope (52°/65°) for the reference.

9:00am **PS2+TF-WeM-4 Quantitative Characterization of Plasma-Induced Defect Creation in InP Substrates Using Conductance Analysis***, **Takahiro Goya,*** Kyoto University, Japan*; Y. Kodama, Y. Zaizen, M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; K. Urabe, K. Eriguchi,* Kyoto University, Japan

To meet increasing demands for higher operating frequency, new material-based systems that exceed the electron mobility limit of Si have attracted attention. InP is one of the promising semiconductors implemented in the next generation devices [1]. In designing the performance, the property degradation during plasma processing—plasma-induced damage (PID) [2]—is a critical issue. However, in contrast to Si devices, there have been no quantitative evaluation technique assessing the nature of PID in InP systems. In this study, we propose a defect characterization technique for InP systems using conductance analysis. N-type InP substrates were exposed to capacitively coupled plasma with Ar gas. Exposure time and peak–to–peak voltage (V_{pp}) were varied from 3 to 30 s and 270 to 450 V, respectively. We first confirmed that the present PID forms damaged layers on Si substrates whose thicknesses were approximately 5 nm by spectroscopic ellipsometry. 5.8 nm SiO_2 films were formed by ALD for electrical analyses. SiO_2/Si structures were prepared in comparison. It was revealed that tunneling current and capacitance-voltage tests (commonly employed in Si devices) were not sufficient to evaluate PID in InP systems. We applied a conductance technique [3] with an optimized equivalent circuit model. An AC modulation bias with a frequency (f_{mod}) from 100 Hz to 1 MHz was superimposed on a DC bias (V_{bias}). The peaks in conductance spectra for the SiO_2/InP devices were found to be "pinned" around 1 kHz after plasma exposure regardless of V_{bias} in depletion, whereas the peak shift in response to V_{bias} was observed for the SiO_2/Si devices. Moreover, the peak intensity for the SiO_2/InP devices increased with V_{pp}, while exposure time did not significantly impact strongly, presumably due to the dose dependence of the profile. These findings indicate that the nature of PID in InP substrates is unique, *i.e.*, the electrical response of created defects is different from that in Si devices. In addition, the PID can be quantified with the conductance method in terms of the peak intensity at a specific f_{mod}. The proposed conductance analysis is extremely useful for the PID assessment in future InP-based devices.

[1] W. R. Deal *et al.*, IEEE IEDM, 2016, p. 707.

[2] K. Eriguchi, J. Phys. D: Appl. Phys. **50**, 333001 (2017).

[3] T. Kuyama *et al.*, Jpn. J. Appl. Phys. **59**, SJJC02 (2020).

9:20am **PS2+TF-WeM-5 Impact of Bias Power and Oxygen Addition on Selective Dry Etching of TiAlC over TiN Using N_2/H_2-based Plasmas***, **Kenji Ishikawa**, T. Nguyen,* Nagoya University, Japan*; K. Shinoda, H. Hamamura,* Hitachi, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High Technologies, Japan*; M. Hori,* Nagoya University, Japan

In the isotropic etching of multiple metal gate materials made of titanium compounds, selectivity of TiAlC against the other materials, involving metal compounds, insulators, and semiconductors, such as TiN, TaN, HfO_2, and C hard mask is required. Wet etching of Ti compounds using H_2O_2 mixtures has been conventional applied. However, this causes damage to the other exposed materials due to low etch rates and insufficient selectivity, as a result of a prolonged treatment time. To increase selectivity of etch rates for TiAlC films, the dry etching for ternary material TiAlC has been developed by processing with high density of radicals generated in a NH_4OH vapor plasma at medium-pressure plasma in our previous study [1]. This is feasible to show a potential of isotropic etching using chemistries containing NH and H.

In this study, selective dry etching of the ternary material TiAlC over TiN has been first developed using N_2/H_2-based plasmas generated from a capacitively coupled plasma etcher at low pressure. Using an *in situ* ellipsometry and an optical emission spectrometer (OES), highly selective etching of TiAlC over TiN has been investigated. In particular, addition of a small amount of O_2 (10%) into the N_2/H_2 plasmas enhanced the selectivity. A process window for selective removal of TiAlC over TiN is presented here at various bias powers, in which chemical etching was dominant at lower bias power with higher selectivity (>5). By using various mixtures of N_2, H_2, and O_2 gases for generating plasmas, surface reactions under energetic ion bombardments produces selective surface modification of the TiAlC and TiN films. Controlling O_2 addition and ion energy is essential for enabling applications of both selective anisotropic or isotropic etching of metal carbides, metal nitrides, or metal oxides.

11:00am **PS2+TF-WeM-10 Bulk Titanium Micromachining and Simultaneous Sidewalls Passivation for Bio-MEMS Applications***, **Rim Ettouri**, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; B. Boutaud, J. Phung, H. Philippe,* MISTIC, France*; R. Dussart,* GREMI CNRS/Université d'Orléans, France

The biomedical field has seen significant expansion because of the rise of microsystems. Even though silicon has historically been the material of choice, improvements in Titanium (Ti) micromachining have enabled the creation of bulk Ti-based devices. Whilst wet etching methods for Ti are available, they are isotropic and so restrict the geometry of features that may be created, especially at the microscopic scale. Conversely, Reactive Ion Etching (RIE) of titanium has allowed the formation of anisotropic profiles and the fabrication of biodevices such as vascular stents and micro-needles for drug delivery. In the literature, three distinct plasma chemistries for titanium dry etching have been reported with promising results: fluorinated, chlorinated, as well as combined chloro-fluorinated plasmas [1].

A method for simultaneous etching and sidewall passivation of bulk titanium is presented, which bypasses the conventional cyclic methods requiring separate passivation steps, such as the MARIO process [2]. Fundamentally enabled by the use of a continuous plasma of $SF_6/O_2/Ar$, the key novelty of this technique lies in the formation of a passivating oxide layer during micromachining . Iridescent oxide colors at the bottom of the etched Ti trenches were obtained, which result from the interference of light reflected from thin transparent oxides. Herein, we explain the oxidation mechanism that occurs during micromachining. Understanding the passivation schemes of Ti RIE is important for increasing feature aspect ratios and further miniaturization of the devices.

By adjusting the plasma parameters, the process can be controlled to achieve the best results in terms of etch rate and anisotropy while maintaining an acceptable undercut. The sidewall passivation material which is formed is found to be a titanium dioxide which contains only minor amounts of fluorine, giving the X-Ray Diffraction (XRD) patterns characteristic of rutile and anatase phases and as shown by the Energy Dispersive X-Ray Spectroscopy microanalyses (EDS). Fundamentally, the corresponding etching profiles strongly correlate the competitive effects based on the simultaneous etching and oxidation of the surface by atomic F and O, respectively.

While an almost infinite number of techniques have been used to form rutile titanium dioxide on any surface, this is yet the first time it has been reported to be achieved by RIE. This can lead to a significant increase in the potential of titanium bio-MEMS and even widen the field of application.

[1] F. Fracassi, R. d'Agostino, Pure and Applied Chemistry 64 (1992) 703-707.

[2] M.F. Aimi et al., Nature Materials 3 (2004) 103-105.

11:20am **PS2+TF-WeM-11 Selective Dry Etching of TiAlC over TiN using N_2/H_2 Plasma Chemistry***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; K. Shinoda, H. Hamamura,* Hitachi, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech, Japan , Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective etching of metal gate materials such as TiAlC over TiN is required in advanced fabrication of fin-type or nanosheet field effect transistor (FET) of logic semiconductor devices. The conventionally wet etching of TiAlC and TiN films using H_2O_2 mixtures causes poor etching performance and device damage. In contrast, dry etching shows advantages in controlling etchant species and their energies for both isotropic and anisotropic processes. In order to obtain higher selectivity between Ti compounds, a non-halogen chemistry for highly selective and controllable dry etching of TiAlC over TiN was reported in our previous study, which developed a feasible dry etching method for ternary material TiAlC using a high-density plasma at medium pressure [1]. For the semiconductor application, in this study, low-pressure dry etching of the ternary material TiAlC has been first developed by using N_2/H_2 plasma.

A capacitively coupled plasma etcher was used to generate N_2/H_2 plasmas, and the upper and lower electrodes were operated with 100 MHz and 2 MHz sources, respectively. Optical emission of an NH molecular line at 336.3 nm from N_2/H_2 plasmas was detected by an optical emission spectrometer (OES). The N_2/H_2 plasma can produce etchant species including NH, N, and H to form volatile products. The etch rate of TiAlC was around 2 nm/min for the N_2/H_2 plasma, whereas no etching occurred with only N_2 plasma or H_2 plasma. Selective etching of TiAlC to TiN has been successfully demonstrated.

The influence of substrate temperature on etch rate and selective etching of TiAlC over TiN was investigated in a range of -20^{o}C to 50^{o}C. The surface modification of the TiAlC and TiN films after plasma exposure was analyzed by X-ray photoelectron spectroscopy (XPS). The XPS analysis revealed that the modified layer that included N-H and C-N bonds formed only on TiAlC and not on TiN. This non-halogen plasmas etchingmethod can be applied for highly selective etching of metal carbides, nitrides, or oxides, based on proposed mechanisms for selective etching of TiAlC over TiN.

[1] T.T.N. Nguyen et al., AVS67, PS-Contributed On Demand-10 (2021).

11:40am **PS2+TF-WeM-12 Surface Modification of CoSi through Interconnect Fabrication Processes***, **Nathan Marchack**, A. Orefice, M. Hopstaken, G. Cohen, C. Lavoie, R. Bruce, C. Chen,* IBM Research

The introduction of copper BEOL interconnects played a critical role in downscaling CMOS technologies. However, at the dimensions required for future technology nodes, this mainstay faces its own set of scaling challenges, such as liner thickness limits and grain boundary scattering. [1] Topological semi-metals possess unique physical properties that make them promising candidates for the next generation of interconnect materials: namely, their resistance-area (RA) product decreases with decreasing thickness. One such material, CoSi is particularly attractive due to its compatibility with existing CMOS integration schemes. [2]

In order to facilitate patterning of semi-metals at competitive node dimensions, it is essential to investigate the influence of fabrication processes (e.g. plasma etching) on the bulk and surface properties. [3] We present surface analysis of subtractive halogen-based plasma etching of CoSi films, including effects on film stoichiometry characterized by XPS. Downstream plasma and wet solution treatments for removal of the damaged surface layers are also presented. It was found that a cyclic approach, comprising alternating exposures of inductively coupled HBr and microwave downstream H_2 plasma, provides the best stoichiometric retention. Finally, the impact of different deposition methods to form CoSi is discussed, with particular focus on the grain size disparities observed.

[1] C.-L. Lo et al., J. App. Phys. 128, 080903, 2020.

[2] C.-T. Chen et al., IEEE Int. Electr. Dev. Meeting, San Francisco, CA, Dec 12-18th, 2020.

[3] N. Marchack et al., J. App. Phys. 130, 080901, 2021.

12:00pm **PS2+TF-WeM-13 PbS Quantum Dots Thin Film Dry Etching***, **Nicolas Le Brun**,* LTM - MINATEC - CEA/LETI, France*; P. Gouraud,* STMicroelectronics, France*; G. Cunge,* LTM - MINATEC - CEA/LETI, France*; L. Parmigiani, S. Allegret-Maret,* STMicroelectronics, France

Nowadays there is an increasing demand to enhance the capabilities of industrial products to sense their environment more efficiently, i.e. under difficult conditions (smoke, darkness…). This challenges semiconductor manufacturers because applications concern many daily life products using image sensors (smartphones, cars, automated tools…etc).

One solution studied recently is to extend the capabilities of image sensors to detect light towards the near Infrared (NIR) and Short-wave Infrared (SWIR) regions . Silicon having weak absorption properties at these wavelengths, manufacturers are looking to develop new materials which could be efficient sensors for these specific regions of the light spectrum.

To this end, quantum dot thin films are promising materials for their tunable band gap, their absorption properties, and their large-scale production availableness.

This study is related to the elaboration of sensors using PbS quantum dot thin films, and will focus on its patterning through a dry etching step. We propose to compare different etch chemistry combinations to define the best etch condition to pattern our PbS quantum dot thin films. In order to ensure the best optical properties of our material, it is crucial to control the slope of the etched profile and to prevent the uncontrolled diffusion of etchant in the quantum dot thin film stack. We will therefore monitor these key parameters under various plasma chemistry combinations as well as other dry etching settings, such as temperature or pressure.

Plasma Science and Technology Division
Room 305 - Session PS1+AP-WeA

Plasma Assisted Atomic Layer Etching

Moderators: Harm Knoops, Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands, **Emilie Despiau-Pujo**, Univ. Grenoble Alpes, CNRS, LTM, France

2:20pm **PS1+AP-WeA-1 Mechanism of Isotropic Plasma Atomic Layer Etching Using Hexafluoroacetylacetone and H_2 Plasma**, ***Nicholas J. Chittock**, J. Maas, M. Merkx, W. Kessels,* Eindhoven University of Technology, The Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, UK*; A. Mackus,* Eindhoven University of Technology, The Netherlands

Interest in atomic scale processing techniques, such as atomic layer etching (ALE), is growing rapidly as accurate thickness control and low damage etching have become necessities in IC fabrication. In this work the mechanism for isotropic plasma ALE of Al_2O_3 using the diketone species hexafluoroacetylacetone (Hhfac) and H_2 plasma is investigated. This alternative process for isotropic plasma ALE could provide improved selectivity for etching metal oxides over Si-based materials.[1,2]

ALE behavior was confirmed using Al_2O_3 planar substrates. Etching is only observed when alternating between Hhfac and H_2 plasma pulses, with the EPC determined to be 1.7 Å/cycle at 350 ˚C, which is higher than the EPC observed for Hacac/O_2 plasma ALE of Al_2O_3.[2] No thickness change was observed on thermally grown SiO_2 with this ALE chemistry, indicating near perfect selectivity between Al_2O_3 and SiO_2.

This process exhibits ALE characteristics; however, the self-limiting mechanism is not fully understood. To investigate the reaction mechanism Fourier transform infrared spectroscopy (FTIR) was employed to observe the different binding configurations of hfac on an Al_2O_3 surface. Two configurations can be determined from FTIR: chelate where both oxygen atoms bind to the same metal atom, or monodentate when only one oxygen is bound.[3] Chelate is the preferred binding configuration; however, for low dose times the majority of measured hfac surface species are in monodentate configuration. It was concluded that chelate species are lost from the surface as volatile metal-diketonate etch products. As dosing continues, the monodentate coverage increases and inhibits chelate binding, and thus etching, which explains the self-limiting behavior. A H_2 plasma pulse in half-cycle B removes the adsorbed hfac, resetting the surface for the next ALE cycle.

In summary the two binding configurations of hfac adsorbates play important and distinct roles: the chelate configuration generates volatile etch products, while the monodentate configuration ensures that the etch is self-limiting. Together these reactions, combined with surface cleaning during half-cycle B, yield an ALE process for Al_2O_3 with excellent selectivity to SiO_2 and a high level of etch control.

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2:40pm **PS1+AP-WeA-2 AVS Dorothy M. and Earl S. Hoffman Awardee Talk: On the Chemical and Physical Mechanisms of Etch Product Volatilization in Plasma Enhanced Atomic Layer Etch of Silicon Nitride with Hydrofluorocarbons**, ***Erik Cheng**[1][2], G. Hwang,* The University of Texas at Austin*; P. Ventzek, Z. Chen, S. Sridhar,* Tokyo Electron America

Low energy ion bombardment is a key part of plasma enhanced atomic layer etch (PEALE) which may induce surface reactions unlikely to occur under thermal conditions, moving such systems far from equilibrium. These processes, however, are uniquely challenging to study both experimentally and computationally, due the critical importance of both complex, non-equilibrium chemistry at atomic length- and timescales, as well as more long-range and sustained physical effects that influence the system beyond individual reactive sites.

We previously presented a novel simulation approach and used it to uncover underlying mechanisms in the ion bombardment step of PEALE of silicon nitride (SiN) with hydrofluorocarbons (HFCs). The key role of two key HFCs, CF4 and CH3F, via formation of a physisorbed monolayer, their ion-induced decomposition, and the resulting differences in etch outcomes were discussed. The details of the formation of volatile etch products, however, were less understood and are the focus of this talk.

We first note that we saw no evidence of thermal volatilization. Ar ion impacts can directly cleave bonds both in the HFC precursors as well as the underlying SiN and critically perform three key functions: 1) generating active species through HFC decomposition, 2) generating active sites on the SiN surface, and 3) enabling structural rearrangement at and near the SiN surface. Through the accumulation of damage, the Si-N bonds keeping Si atoms bound to the surface are broken over time, with coordination defects often being passivated by C, H, and F. Through this, the Si becomes more weakly bound to the surface and is thus more likely to be etched. However, many volatile fragments contain at least one N atom, suggesting that it is not always necessary to cleave all Si-N bonds for volatilization to occur. This could be associated with fragment production essentially always resulting from effects of an ion impact. For fragmentation induced by a direct Ar impact, these tend to be highly chaotic processes characterized by sputtering-like behavior, often generating multiple reactive fragments in one area that combine to form a free fragment. These events may allow a variety of surface conditions to yield etch products. We also see evidence of "secondary events" where ion impact releases a small reactive ion (for example, Si-F -> Si + F) which can impact a weakly bound moiety elsewhere on the surface to form a free fragment. These events appear to be more sensitive to surface conditions. Understanding these two key volatilization pathways may be the key to unlocking far finer levels of control over the PEALE process than currently achievable.

3:00pm **PS1+AP-WeA-3 Use of Atomic Layer Etching Techniques in Todays and Tomorrows Industry**, ***Dominik Metzler***, IBM Research Division, Albany, NY **INVITED**

Atomic Layer Etching and Quasi Atomic Layer Etching processes have gained a lot of traction and application throughout the last years. However, not everything described as ALE is a true atomic layer process in its strict definition. We will first discuss the use and definition of various cyclic process and compare to pulsed processes, the process regime of which can differ significantly. In a more general consideration, the approach of reactant control, as the core of ALE, is additionally employed in various other applications that are not QALE. Subsequently, we will highlight and describe specific use cases for which such processes have been explored and implemented at IBM Research in Albany. Fin patterning is a major example of QALE yielding major improvements in profile and CD control during RIE. Additionally, QALE allowed enhanced selectivity during self-aligned contact etches, crucial to its success. For S/D recess possible benefits are expected in a similar fashion. While many of the applications focus on the FEOL, there are also applications of cyclic processes, or QALE-like, in the BEOL, such as Photoresist protection and CD control.

4:20pm **PS1+AP-WeA-7 Approaches to Improve the SiO_2 to SiN_x Etch Selectivity during ALE and RIE**, ***Xue Wang***, Colorado School of Mines*; R. Gasvoda, P. Kumar, E. Hudson,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

In plasma etching, the etch selectivity of SiO_2 relative to SiN_x can be controlled by tuning process parameters such as the fluorocarbon or hydrofluorocarbon feed gas, dilution with other gases such as H_2 or O_2, and by tuning the ion flux and the ion energy distribution. Previously, we showed that selective functionalization of plasma-deposited SiO_2 or SiN_x with hydrocarbons can be used to enhance etch selectivity. Building on our previous work, using in situ optical surface diagnostics, we will show that this approach can be extended to atmosphere-exposed and partially-etched SiO_2 and SiN_x surface during atomic layer etching (ALE). In addition, we have also studied the mechanism for the enhancement in etch selectivity for SiO_2 over SiN_x by increasing the substrate temperature during reactive ion etching (RIE).

In our previous work, we demonstrated that pre-functionalization of a pristine plasma-deposited SiN_x surface with benzaldehyde accelerates the formation of a graphitic hydrofluorocarbon layer during C_4F_6/Ar plasma-assisted ALE, and lowers the loss of SiN_x prior to complete etch stop. However, after exposure to atmosphere, SiN_x forms a SiO_xN_y layer with surface –OH groups similar to SiO_2. On the other hand, partially-etched SiO_2 and SiN_x surfaces have a residual CF_x layer, which is very reactive with most hydrocarbon molecules. Herein, using in situ ATR-FTIR spectroscopy, we

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

[2] **AVS Dorothy M. and Earl S. Hoffman Awardee**

demonstrate this pre-functionalization approach can be extended to technologically relevant surfaces by removing the surface SiO_xN_y layer in one ALE cycle while minimizing the CF_x residue on the SiN_x and SiO_2 surfaces: this allows for selective benzaldehyde attachment to the SiN_x surface. In subsequent ALE cycles, we show that the selectivity for benzaldehyde attachment to SiN_x over SiO_2 reduces with the slow accumulation of a carbon-rich residue on both surfaces. Using in situ 4-wavelength ellipsometry, we show that benzaldehyde dosing after the 1st ALE cycle reduces the amount of SiN_x etched and increases the etch selectivity from 1.7 to 2.1 after 20 ALE cycles. If we introduce a second benzaldehyde dose after the 5th ALE cycle, which is prior to significant CF_x accumulation on SiO_2, the selectivity further improved from 2.1 to 3.4.

Finally, we also studied the mechanism for the substrate temperature dependence on the etch selectivity of SiO_2 to SiN_x during C_4F_6/Ar plasma RIE. Our in situ optical diagnostics show that increasing the substrate temperature during RIE of SiN_x from 70 to 120 °C accelerates the formation of a graphitic CF_x layer, while there was no noticeable effect over the same temperature range during RIE of SiO_2.

4:40pm **PS1+AP-WeA-8 Plasma Atomic Layer Etching of Molybdenum with Fluorocarbon and Hydrofluorocarbon***, **Yongjae Kim**, H. Kang, H. Ha, H. Chae,* Sungkyunkwan University, Korea

Copper is widely used for interconnect lines in semiconductor devices, and the resistivity of copper is rapidly increasing as the critical dimension shrinks below 30nm. [1] Dual damascene process based on copper have reached limits due to the continuous shrinkage of critical dimensions. Semi damascene process is an alternative technique, and metal is patterned by reactive ion etching (RIE). [2] Conventional plasma etching process has limitations in uniformity, surface roughness. Atomic layer etching (ALE) process has advantages of good uniformity, smoother surfaces, and precise thickness control than conventional reactive ion etching process.

In this work, ALE process was performed for molybdenum in an inductively coupled plasma (ICP) reactor. The ALE process consists of two steps: surface modification with fluorine contained plasma and ion bombardment with Ar plasma. In the first step, the fluorocarbon layers are deposited on molybdenum surface with C_4F_8 or CHF_3 plasmas. In the second step, the modified layers are etched with ions from Ar plasma. Molybdenum ALE process was performed with changing Ar plasma bias voltage at 50~350V, and the ALE window that constant etch rate region was confirmed with bias voltage of 100~230V. Etch rate of cobalt was self-limited at the Ar plasma time of 3 minutes. The etch rate of molybdenum controlled below 1 nm/cycle. The surface roughness was compared RIE process and ALE process, and the surface roughness of the ALE process was lower than that of the RIE process.

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Keywords: Atomic layer etching, Molybdenum etching

5:00pm **PS1+AP-WeA-9 Atomic Layer Etching of Si by Surface Chlorination, Ar or He Sputtering***, **Tao Li**, E. Miller,* IBM Research Division, Albany, NY*; S. Schmitz, P. Friddle, W. Yang,* Lam Research Corporation

Anisotropic etching of silicon with active fin heights of 45nm or greater is critical for fin patterning and continuous CMOS scaling. Tight control of fin CD and taper is critical for the device, in particular channel control. In addition, uniform etching of iso/dense features and accurate pattern transfer across various fin dimensions require Si etching to enter atomic level control. In this IBM and Lam collaborative study, we evaluated the impact of He and Ar sputter as well as silicon nitride and silicon oxide hard mask (HM) on selectivity and Si profile. We find that nitride HM tends to be less resilient than oxide HM as sputter energy increases. For both He and Ar ALE, we explored the influence of ion-angle-scattering on fin profile as well as various surface protection methods to address ion-angle-scattering side-effect. We will also examine Ar ALE at low bias.

5:20pm **PS1+AP-WeA-10 Real-Time Monitoring of Atomic Layer Etching in Cl_2/Ar Pulsed Gas, Pulsed Power Plasmas by Optical Emission Spectroscopy***, **Qinzhen Hao**, V. Donnelly,* University of Houston*; S. Nam, H. Yoon,* Samsung Electronics, Republic of Korea

Optical emission spectroscopy was used as a real-time monitor of atomic layer etching (ALE) of Si in an Ar inductively-coupled (ICP) plasma. Pulses of Cl_2 gas were repetitively injected into a continuous flow of Ar, followed by simultaneous ignition of the ICP and application of substrate rf bias power (either continuous, or rapidly modulated) for 10s. Optical emissions in the UV from Si, SiCl, $SiCl_2$, $SiCl_3$ and Ar^+, and in the far-red from Ar and Cl were monitored as a function of time during the bias period, as well in the ICP after the bias power was extinguished. By monitoring emission along a line parallel and close to the substrate surface, and operating at high Ar flow rates, and from an analysis of the time dependencies of the decays of emissions during the bias period, it is argued that emissions are mainly from the primary products sputtered by the energetic Ar ions. Products decay with different, non-exponential time signatures. Cl rapidly decays to undetectable levels early in the bias period, indicating some sputtering of Cl (and/or Cl_2) from the top surface, while Si emission decays more slowly to a nearly constant level, indicative of physical sputtering after sub-surface Cl is nearly depleted. $SiCl_2$ emissions decay to nearly undetectable levels toward the end of the bias period. SiCl emission follows a decay profile between that of Si and $SiCl_2$. Relative emission intensities increased strongly with increasing bias power (self-bias voltages of -30 to -200 V_{DC}), but only moderately with Cl_2 pulse durations (1 to 16s). The ALE products are depleted in $SiCl_2$ and especially $SiCl_3$ relative to etching with constant Cl_2/Ar flows and continuous ICP and bias powers.

5:40pm **PS1+AP-WeA-11 Self-Limited Cyclic Etching of Copper Thin Films in Hydrogen and Argon Plasmas for Copper Hybrid Bonding***, **Qi Wang**, C. Netzband, G. Gibney, S. Voronin, S. Han, S. Arkalgud, P. Biolsi,* TEL Technology Center, America, LLC*; C. Vallee,* College of Nanoscale Science and Engineering, SUNY Polytechnic Institute

Cu/Cu hybrid bonding for 3D integration relies on nanometer level control of copper pad recess depth to create proper and reliable electrical contacts. While the recess can be achieved through chemical mechanical planarization (CMP), as feature size shrinks both Cu and dielectric polish at the same rate, resulting in planar contact pads which severely limits the process window. In this work, we report the atomic layer etch (ALE) of Cu with high selectivity to silicon oxide to supplement CMP for tight recess control across the wafer. Each cycle consists of a H_2 plasma modification step followed by directional removal of the hydrogenated layer by low energetic Ar ions. Precise ion energy control was achieved by applying a DC pulse waveform at a given voltage (energy) to the target (1µs ON time and 2µs OFF time per period). In situ ellipsometry measurements reveal self-limiting removal of material at an etch rate of ~3–4 Å/cycle for the first ALE cycle. As the number of the ALE cycles increases, the amount of material etched per cycle decreases, which is due to the modification of the initial surface roughness condition. After modification of the initial surface, the Cu film is less sensitive to the H_2 plasma and leads to decrease in etch amount per cycle. This can be recovered by physical sputtering of the surface by energetic Ar ions or by introduction of an additional modification step prior to each ALE cycle, resulting in process linearity restoration. Real time mass spectral analysis of the plasma of each etch cycle demonstrates the majority of volatile by-product is in the form of CuH_x and shows excellent correlation with the ellipsometry trends. Additional surface characterization by in vacuo XPS and AFM will be discussed.

6:00pm **PS1+AP-WeA-12 Examination of Mechanisms and Processes of Atomic Layer Etching of Copper***, **Taylor Smith**,* University of California, Los Angeles*; E. Crumlin,* Lawrence Berkeley National Laboratory*; J. Chang,* University of California, Los Angeles

Copper is the primary material used for the interconnects of an integrated circuit (IC). The dual damascene process was initially developed to deposit and pattern copper due to the difficulties of using traditional dry etching techniques, but the dual damascene process is reaching its practical limits. Atomic layer etching (ALE) is emerging as a process that could help replace the dual damascene process. In this work, we examine a plasma-thermal ALE process that uses plasma modification followed by a formic acid (FA) vapor phase removal step. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to examine the FA vapor exposure step in particular detail. These *in operando* measurements aided in proposing the surface reaction mechanism of the modified copper surface during the vapor phase removal.

In addition, a nitrogen plasma was used to develop an ALE process based on nitridation of the copper film. Previous ALE of copper has used oxidation as the first modification step—however, copper spontaneously oxidizes on ambient exposure, making it difficult to decouple the effects of the process from ambient exposure. On the other hand, copper nitride does not form spontaneously on exposure to ambient conditions, so all nitridation is a direct result of processing. Plasma nitridation of copper has been accomplished using an ICP reactor with a nitrogen plasma, and the resulting copper nitride film has been characterized by XPS. The copper nitride film has an approximate composition of $CuN_{0.3}$.

Plasma Science and Technology Division

Room 315 - Session PS2+SE-WeA

Atmospheric Pressure Plasmas and their Applications

Moderators: Adam Pranda, TEL Technology Center, America, LLC, **François Reniers**, Université Libre de Bruxelles, Belgium

2:20pm **PS2+SE-WeA-1 Organized DBD Streamers for Maskless Chemical and Topographic Patterning of Surfaces***, O. Polonskyi, T. Hartig,* UCSB Chemical Engineering*; J. Uzarski,* U.S. Army Combat Capabilities Development Command Soldier Center*; **Michael Gordon**,* UCSB Chemical Engineering

Current methods for plasma-based modification of material surfaces (e.g., etching; modifying adhesion, surface chemistry, or wettability; and deposition) cannot often deliver precise control over the location of treatment without extensive use of complex lithographic or photoresist masks. Dielectric barrier discharge (DBD) plasmas operating at atmospheric pressure can accomplish such surface treatments through the creation of random plasma filaments or 'streamers' where surface treatment preferentially occurs. Unfortunately, spatially random and intermittent formation of plasma streamers usually precludes precise patterning.

In this work, we demonstrate how DBD streamers can be sufficiently controlled, via self-organization (with voltage and frequency) and more specifically with topographically patterned dielectrics and raster-scanning of a single streamer, to accomplish localized and user-defined spatial treatment of various substrates without the use of lithographic masks. Spatially organized DBD steamers were used to locally modify the wettability (hydrophilic vs. phobic character) and chemistry of various material surfaces (PMMA, nylon, Teflon, glass, metals), as well as modify surface roughness and etch. Contact angle, XPS, AFM, IR and Raman mapping before and after treatment reveal that surface chemical changes occur preferentially where streamers form, and moreover, that streamer exposure can be tailored to achieve different kinds of multifunctional surfaces. Examples to be highlighted include (i) maskless etching of PMMA on Si at specific locations, (ii) creating bio-inspired chemical patterns on glass to mimic insect carapaces with differential wetting, (iii) rendering Teflon hydrophilic at precise locations, and (iv) creating surfaces with orthogonal wetting characteristics (e.g., simultaneously hydrophilic and phobic over different length scales).

3:00pm **PS2+SE-WeA-3 An Atmospheric-Pressure Microwave Plasma Source for "Chemical Waste-Free" Surface Cleaning and Anti-Corrosion Coatings***, D. Ellis,* University of Illinois at Urbana-Champaign*; D. Krogstad,* Applied Research Institute, University of Illinois at Urbana-Champaign*; M. Sankaran, **David Ruzic**,* University of Illinois at Urbana-Champaign

Metals such as steel are widely used in infrastructure, transportation, and manufacturing where they are exposed to corrosive environments. While higher grade metal alloys can have lower corrosivity, they have significantly higher cost. A potentially more cost-effective approach is to protect metals from corrosion by protective coatings. Currently, many of the best protective coatings require application through expensive dip tank processes that result in a high amount of chemical waste that can be potentially hazardous and result in significant waste remediation costs. For this reason, there is a need to develop a low-cost, low-chemical waste process to apply protective coatings to a variety of metals, including mild steel.

We have developed an atmospheric-pressure microwave plasma for the cleaning and coating of metal surfaces. By relying predominantly on gases, such as air or nitrogen, with aerosolized precursors instead of wet chemicals, chemical waste is greatly reduced. Here, we present a study of 1008/1010 mild steel. Cleaning of surfaces was demonstrated by purposefully contaminating with oil or sodium chloride. Following plasma treatment, the surfaces were characterized by Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering spectroscopy (RBS). In the case of salt, a Bresle test was also employed. We find that the plasma is very effective in removing oil, with no hydrocarbons being detected on the treated surface through FTIR measurements. Plasma treatment is also found to be capable of removing thin layers of salt, including residual salt left after rinsing surfaces with water. We have also shown that the atmospheric pressure plasma can be used to deposit nanoscale silica coatings onto the steel substrates to promote corrosion protection and paint adhesion. Films were deposited by introducing tetraethylorthosilicate (TEOS) vapor in the plasma. The film properties, including composition and thickness, were characterized by scanning electron microscopy, FTIR, and RBS. Electrochemical testing was used to determine the corrosion protection properties of the films, while accelerated corrosion testing using salt fog was used to determine the corrosion prevention capability of the film under a compromised paint barrier. Plasma-deposited silicon oxide films were found to substantially decrease corrosion.

3:20pm **PS2+SE-WeA-4 Characteristics of Ionization Wave Propagation on Variable Thickness Dielectric Substrate***, **Joshua Morsell**, S. Shannon,* North Carolina State University

The interaction of atmospheric pressure plasma jets (APPJ's) with various materials and material topologies can greatly influence an array of existing and new plasma based applications.One area of interest is the ionization waves that are generated by these plasma jets. These ionization waves provide consistent and repeatable application of fields and excited species to the target surface. The focus of this work is to study the effect of dielectric thickness on the propagation of ionization waves as they impinge upon the target surface.

The plasma source in question is an APPJ with helium as the working gas as used in [J. Jiang et al., PSST29(2020), 045023]. The work presented utilizes a nanosecond DC pulse of positive polarity. Pulse width is 500 ns with voltage ranging from 3.5-4.5 kV. Voltage and current data is collected via integrated current probe and a high voltage probe at the source head. The dielectric surfaces consist of two experimental configurations. The first is a 3-D printed stage with a metal foil ground plane. Microscope cover glass 150 micron thick is stacked on this stage to provide a dielectric surface from 0.15 – 3.0 mm thick. The cover glass is 24x24 mm. The second configuration is a 3-D printed stage where the ground plane is a 50 mm square glass plate 1.1 mm thick with conductive ITO deposited on one side. 1 mm thick microscope slides are used to make a dielectric surface of 1.1-10.1 mm thick. Both configurations have a constant gap between the source tip and dielectric surface of 10.5-11mm. A PI-MAX 3 ICCD camera is used to image the ionization wave interaction with the target dielectric. The ICCD is gated to 5 ns and a 5 ns delay time step.

For both experiments, the surface wave velocity has a strong dependence with dielectric thickness, increasing by a factor of three from 0.15mm to 1.65mm.For thicknesses greater than 1.65mm the velocity remains relatively constant for measurements out to 10mm thickness. Surface velocity ranges from 1.5-4.5*10^4 m/s. It is noted that the initial conditions for each dataset is kept constant by ensuring that the velocity of the impinging axial ionization wave is constant. Axial velocities for the fine and bulk studies are 1.88*10^5 m/s and 1.81*10^5 m/s, respectively. These results suggest a transition in electric field structure as the axial component of the impinging wave dissipates into the dielectric bulk more readily than the radial field with a maximum penetration depth that eventually saturates the velocity of the surface wave.

This work is supported as part of the Department of Energy Center for Plasma Interactions with Complex Interfaces (PICI).

5:00pm **PS2+SE-WeA-9 Synthesis and Applications of Metal Oxides NPs***, **Davide Mariotti**,* University of Ulster, UK **INVITED**

Metal oxides are an extraordinary class of materials that have found wide applicability for a number of century-defining technologies (e.g. flat-panel display, capacitors and energy storage) mainly due to their dielectric properties and chemical inertness. Doping, defect engineering, quantum confinement and extending to clusters, ternary or high entropy oxides can create disruptive materials with new or improved properties. Atmospheric pressure microplasmas represent a viable synthesis platform to achieve exceptional tuning capability therefore achieving an exquisite control of the size, composition and defects of metal oxide nanoparticles [1-4]. In this contribution we will show how microplasmas can offer a generalized methodology for the synthesis of metal oxide nanoparticles and produce very desirable opto-electronic properties. Therefore we will discuss the formation of metal oxide nanoparticles with gas-phase microplasmas as well as hybrid plasma-liquid systems [5-10]. We will further provide an overview of their application opportunities in energy-related applications as well as other disciplines [8-9]. Examples will include oxides from Ni, Cu, Mn, Sn, Co, Mo and Zn. Finally we will provide future directions at the boundaries between ordered and disordered crystal structures.

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5:40pm **PS2+SE-WeA-11 AVS Graduate Research Awardee Talk: Immobilization of Plasma Filaments in a DBD: Discharge Characterization and Patterned Coating Deposition***, **Annaëlle Demaude**[1,2], A. Remy, D. Petitjean, J. Zveny,* Université libre de Bruxelles, Belgium*; K. Baert, T. Hauffman,* Vrije Universiteit Brussel, Belgium*; E. Goormaghtigh,* Université libre de Bruxelles, Belgium*; M. Gordon,* University of California Santa Barbara*; F. Reniers,* Université libre de Bruxelles, Belgium

Dielectric barrier discharges (DBDs) can be ignited in different discharge modes: glow, homogeneous or filamentary. At atmospheric pressure, in most gases, the latter mode is more often obtained than the others. Filamentary DBDs are characterized by the presence of micro-discharge channels (filaments), which are very short-lived (few ns) and ignite randomly in the interelectrode space.[1] This can be seen as a drawback for surface functionalization/thin film deposition by DBDs, as it can lead to inhomogeneous treatments.[2] Instead of avoiding these filaments, their higher density in current and energetic species was recently exploited to locally modify surfaces. This was achieved using auto-organized filamentary DBDs or directly by immobilization of the filaments.[3,4] Using this latter method, our team has extended the concept further to the deposition of patterned thin films.[5]

In this work, control over the ignition location of the filaments has been achieved in Ar and in N_2 by texturizing one of the dielectric surfaces to locally favor the ignition of the micro-discharges. The distribution of the filaments in the discharge gap and their electrical properties were examined by high-speed camera imaging and by electrical measurements, respectively. By injecting different precursors such as propargyl methacrylate (PMA) or vanadium(V) oxide triisopropoxide in the Ar or N_2 immobilized filaments, hydrophilic/phobic patterned surfaces or crystalline vanadium oxide (VO_x) patterns were obtained, respectively. The spatial differences in chemistry, morphology, wettability (for PMA films) and crystallinity (for VO_x films) of the deposited films were investigated by micro-XPS and micro-IR analysis, by profilometry, water contact angle measurements and XRD, respectively. The properties of the deposited films and of the corresponding discharges could then be correlated.

This opens a new route for the deposition of patterned coatings in a one step-process at atmospheric pressure and could contribute to a better understanding of chemical reactions occurring in filamentary DBDs.

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6:00pm **PS2+SE-WeA-12 Maximizing Photon Flux in a Miniaturized Photoionization Detector***, **Mackenzie Meyer**, X. Huang, A. Sivakumar, X. Fan, M. Kushner,* University of Michigan

Photoionization detectors (PIDs) use wavelength specific UV and VUV radiation to selectively ionize, for example, volatile organic and inorganic compounds (VOCs and VICs). These compounds are then detected by collecting the resulting ion current. Miniature PIDs are of interest for lab-on-a-chip applications. A miniature PID has been developed in which VUV photons are produced by a pulsed He atmospheric pressure plasma generated in a double dielectric barrier discharge (DBD). Maximizing the fluence of photons that reach the analyte inlet will increase performance of the PID, lowering the detection limit or increasing speed of operation. The operation and optimization of a DBD-PID with the goal of increasing photon fluence were computationally investigated using the 2-dimensional model *nonPDPSIM*. Several strategies were identified to increase the photon fluence. For example, making the powered electrode V-shaped instead of flat increased the photon fluence, as the electric field is enhanced at the tip of the powered electrode. Using an array of powered electrodes capable of sustaining multiple streamers also increased the photon fluence, as did positioning the electrodes closer to the analyte inlet. The most substantial increase in photon fluence came from increasing the capacitance of the bounding dielectric by increasing the relative permittivity from 10 (typical of conventional fabrication materials) to 300 (for specialized materials). Increasing the capacitance of the dielectric increased the voltage drop across the plasma and stabilized the plasma filament while increasing current for a given voltage

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Advanced Surface Engineering Division
Room 317 - Session SE+MN+PS+TF-WeA

Vapor Deposition Technologies and New Trends in Surface Engineering

Moderators: Jianliang Lin, Southwest Research Institute, **Filippo Mangolini**, The University of Texas at Austin

2:20pm **SE+MN+PS+TF-WeA-1 Breaking the Back-Attraction by Bipolar HiPIMS Bursts***, **Rajesh Ganesan**,* University of Illinois at Urbana-Champaign **INVITED**

Limiting the back-attraction of ions is crucial to increase the deposition rate in HiPIMS processing. Back-attraction can be considerably limited by bipolar plasma bursts in which a positive voltage pulse is applied instantaneously after the negative voltage pulse. Energy-resolved mass spectroscopy confirms that, in addition to the increased flux, the energy of the target metal ions travelling from the target to the substrate is also increased, as a function of positive pulse length. Amorphous carbon coatings have been deposited by bipolar HiPIMS (BiPIMS) as a case study. The increased energy of the depositing flux led to a higher density of the carbon coatings and a significant reduction in the incorporation of the sputter gas atom, argon, was observed in the coatings. Langmuir probe measurements suggest the optimum plasma density window to minimize arc generation and reduce the probability of generated arcs moving away from the target racetrack, which results in smoother coatings. BiPIMS voltage pulses of optimized length and magnitude help to coat high quality amorphous carbon coatings with excellent machining functionalities.

3:00pm **SE+MN+PS+TF-WeA-3 Experimental and Theoretical Study of the Thermal Shock Behavior of MAX Phase Thin Films***, **Matej Fekete**, C. Azina, P. Ondračka, L. Löfler, D. Bogdanovski,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; M. Hans, J. Schneider,* RWTH Aachen University, Germany

Components subjected to rapid temperature changes are prone to thermal shock, which may result in damage or catastrophic failure. Thus, thermal shock resistance is one of the performance-defining properties for an application where extreme temperature gradients are required. The thermal shock resistance can be described by the thermal shock parameter (R_T), which depends on the flexural strength, thermal conductivity, Poisson's ratio, linear coefficient of thermal expansion, and elastic modulus. In this study, these thermomechanical properties of Ti_3AlC_2 and Cr_2AlC MAX phase coatings are investigated by both experiment and theory. The R_T of Ti_3AlC_2 obtained through quantum mechanical predictions is in good agreement with the experimentally obtained R_T. However, for Cr_2AlC, the theoretical predictions result in approximately two times larger

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

[2] **AVS Graduate Research Awardee**

R_T than experiments. This difference may be caused by omitted spin-polarization in the calculation of the electronic part of the thermal conductivity. Correlating the studied MAX phase thin films, both experiments and theory indicate superior facture behavior of Ti_3AlC_2 in comparison to Cr_2AlC. This is attributed primarily to the higher thermal conductivity of Ti_3AlC_2.

4:20pm **SE+MN+PS+TF-WeA-7 Combinatorial Application of Advanced Characterization Methods to Illuminate the Role of Interfaces in Multilayer Coatings***, **Nina Schalk**, C. Kainz, F. Frank,* Montanuniversität Leoben, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; M. Tkadletz,* Montanuniversität Leoben, Austria **INVITED**

The microstructural characterization of multilayer coatings and their interfaces is challenging, especially if the layer thicknesses are only in the nm range. Within this talk, two model coatings are used to evaluate the suitability of several characterization methods for the investigation of their microstructure and interfaces on different length scales. The fine grained cathodic arc evaporated ZrN/TiAlN and the rather coarse grained chemical vapor deposited TiCN/TiC multilayer model coatings exhibit different bilayer thicknesses and layer thickness ratios and thus allow also insight into the effect of the layer thickness on coherency, grain size and strain state. Starting with methods such as scanning electron microscopy and laboratory X-ray diffraction, an overview of the coating structure and information on the average strain/stress state can be obtained. Depending on the grain size and individual layer thickness, high resolution electron backscatter diffraction allows a more detailed insight into the microstructure and strain state of individual layers. In addition, information about gradients of strain/stress across the coating thickness is accessible by cross-sectional X-ray nanodiffraction. However, for a detailed investigation of the interfaces, the application of high resolution methods such as transmission electron microscopy and atom probe tomography is indispensable, providing information about lattice misfits and related strain evolution in the layers as well as on the sharpness of the interfaces in terms of elemental distribution down to the atomic scale. The present talk highlights that for the characterization of the different multilayer systems the combinatorial application of different characterization methods is possible and reasonable.

5:00pm **SE+MN+PS+TF-WeA-9 Influence of Al-Content on Structure, Mechanical Properties and Thermal Stability of Reactively Sputtered AlTaTiVZr High-Entropy Nitride Coatings***, **Alexander Kirnbauer**[1]*, TU Wien, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Austria

In the field of materials research, a novel alloying concept, so-called high-entropy alloys (HEAs), has gained particular attention within the last decade. These alloys contain 5 or more elements in equiatomic or near-equiatomic composition. Properties, like hardness, strength, and toughness can be attributed to the specific elemental distribution and are often superior to those of conventional alloys. In parallel to HEAs also high-entropy ceramics (HECs) moved into in the focus of research. These consist of a solid solution of 5 or more binary nitrides, carbides, oxides, or borides. Within this work, we investigate the structure and, mechanical properties of thin films based on the high-entropy concept, with particular emphasis on the thermal stability, dependent on the Al content in AlTaTiVZr thin films.

Therefore, AlTaTiVZr nitride coatings were reactively sputtered in a lab-scale sputter deposition facility using a single powder-metallurgically produced composite target and Al cubes placed along the racetrack to increase the Al content within the coatings. The coatings in as-deposited state show a fine-columnar growth and crystallise in a single-phase face-centred cubic (fcc) structure. The hardness of our coatings in as-deposited state is ~32.8 GPa and relatively independent on the Al-content. We studied the influence of the Al content on the thermal stability by investigating the structural evolution of our coatings by DSC and powder X-ray diffraction, as well as nanoindentation upon vacuum annealing. The study reveals a distinct influence of the Al-content on the decomposition of the solid solution into an fcc-matrix and Al-rich domains.

5:20pm **SE+MN+PS+TF-WeA-10 Ternary Transition Metal Diborides – Future Defect Engineered Protective Coating Materials?***, A. Hirle, L. Zauner, C. Fuger, A. Bahr, R. Hahn, T. Wojcik, T. Glechner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; **Helmut Riedl**,* TU Wien, Austria

In the progression of novel protective thin film materials, the attention for transition metal diborides (TMB_2) substantially increased during the last years. The unique strength of their hybridized covalent bonds combined with their hexagonal close-packed (hcp) structures is a big advantage and limiting factor at the same time. The related brittleness, variety of crystal structures, and stoichiometries depict significant challenges for a broad usage of these structurally imperfect coating materials. Furthermore, the formation of non-adherent and volatile oxide scales is also a major limiting factor.

Within this study, we want to address these specific challenges on various ternary model systems within group IV to VI transition metal diborides (e.g. $TM_{1-y}X_yB_{2\pm z}$ prototypes). As structural defects play a major role for the phase formation of the two characteristic hexagonal structure types (α–AlB_2 vs. ω-W_2B_{5-x}-prototype), the target composition and ionization degree within the plasma, has been systematically correlated with the deposition parameters for non-reactive DCMS and HiPIMS depositions. In addition, different alloying concepts for enhancing the ductile character – by microstructural design of imperfect grain boundary structures [1, 2] – as well as oxidation resistance – up to 1200 °C through Si alloying [3] – of these superhard ternary diborides will be discussed in detail. To describe all these relations comprehensively, we correlated the synthesis parameters with structural and morphological evolution using XRD, HR-TEM, APT, as well as micro-mechanical testing methods. Furthermore, specific aspects have also been described by atomistic modelling (DFT).

Keywords : Ternary Borides; Protective Coatings; Defect Engineering; High Temperature Oxidation;

[1]T. Glechner, H.G. Oemer, T. Wojcik, M. Weiss, A. Limbeck, J. Ramm, P. Polcik, H. Riedl, Influence of Si on the oxidation behavior of TM-Si-B2±z coatings (TM = Ti, Cr, Hf, Ta, W), Surf. Coat. Technol. 434 (2022) 128178.

[2] C. Fuger, R. Hahn, L. Zauner, T. Wojcik, M. Weiss, A. Limbeck, O. Hunold, P. Polcik, H. Riedl, Anisotropic super-hardness of hexagonal WB2±z thin films, Materials Research Letters. 10 (2022) 70–77.

5:40pm **SE+MN+PS+TF-WeA-11 Influence of Interplay of Substrate Template Effects and Bias Voltage on the Microstructure of Cathodic Arc Evaporated Fcc-$Ti_{0.5}Al_{0.5}N$ Coatings***, **Michael Tkadletz**, N. Schalk, H. Waldl,* Montanuniversität Leoben, Austria*; B. Sartory, J. Wosik,* Materials Center Leoben Forschung GmbH, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria

Ever since the implementation of hard coatings as wear protection for cutting tools, their microstructural design has been of major interest. While the effect of the deposition parameters, such as the applied bias voltage or the substrate temperature, on the microstructure are frequently investigated and rather well understood, commonly less attention is paid to the used cemented carbide substrates. Yet properties like their phase composition and carbide grain size significantly influence the resulting coating microstructure. Thus, within this work substrate template effects are studied on fcc-$Ti_{0.5}Al_{0.5}N$ coatings grown by cathodic arc evaporation onto cemented carbide substrates with different WC grain sizes. A systematic variation of the bias voltage resulted in coarse, intermediate and fine grained coating microstructures, which revealed substrate template-based coating growth at low bias voltages and bias dominated coating growth at high bias voltages. In addition, a strong influence of the applied bias voltage on the resulting preferred orientation of the deposited coatings was observed, providing the basis to tailor the texture to 100, 110 or 111. Elaborate X-ray diffraction and electron microscopy studies contributed to gain further understanding of the substrate template effects and revealed that implementation of a suitable baselayer offers the possibility to effectively prevent any influence of the used substrate on the microstructural evolution of the coating. Supplementary micromechanical experiments illuminated the impact of microstructure, template and non-template based coating growth on the obtained mechanical properties. The obtained results set the fundament to implement tailored microstructures with designed gradients of crystallite size, preferred orientation and consequently mechanical properties, which, as required, either utilize substrate template effects or avoid them.

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[1] **2021 ASED Young Investigator Awardee**

6:00pm **SE+MN+PS+TF-WeA-12 Super Hard High Temperature TaC-Based Superlattice Protective Coatings Prepared by Magnetron Sputtering***, **Barbara Schmid,*** TU Wien, Austria*; S. Kolozsvari,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Austria

Transition metal carbides belong to ultra-high temperature ceramics (UHTC) and are particularly valued for their high thermal and mechanical stability as well as melting points of even above 4000 °C. Therefore, those materials are especially interesting for the application as protective coatings. However, a considerable limitation of these materials is their high inherent brittleness. Inspired by the success of nanolayered superlattice architecture—shown to enhance both hardness and toughness of transition metal nitrides like TiN/CrN or TiN/WN—we developed superlattice films based on TaC. These combinations are motivated by ab initio density functional theory calculations exhibiting large and small shear modulus and lattice parameter misfits. Our coatings are prepared via non-reactive DC and pulsed DC magnetron sputtering using binary carbide compound targets. In our study, we want to compare TaC-based superlattice systems and investigate the influence of the superlattice architecture on material characteristics like mechanical, thermal and electrical properties. Apart from nanoindentation and micromechanical cantilever testing for hardness and fracture toughness, material stability at elevated temperatures as well as thermoelectrical properties are being characterized.

Plasma Science and Technology Division
Room 315 - Session PS-ThM

Plasma Processing for Advanced Semiconductor Devices

Moderators: John Arnold, IBM Research Division, Albany, NY, **Kenji Maeda**, Hitachi High Technologies America Inc.

8:00am **PS-ThM-1 Dry Etch Solution to a Challenge in Si/SiGe Dual Channel Process Integration**, ***Yohei Ishii***[1], Hitachi High-Tech America, Inc.; *R. Sugano,* Hitachi, Ltd., Japan; *Y. Lee, W. Wu,* Taiwan Semiconductor Research Institute, Taiwan; *L. Kovatch,* Hitachi High-Tech America, Inc.; *K. Maeda, M. Miura,* Hitachi High-Tech Corporation, Japan **INVITED**

Continuous improvement in terms of device scaling has been made in order to follow Moore's law. Transition from planar structure into Fin-type Field Effect transistor (FinFET) was incorporated so as to obtain higher drive current and lower leakage. To further enhance the electrical properties, introduction of high mobility channel material in P-FET [1], silicon germanium (SiGe), was utilized, while maintaining silicon (Si) in N-FET. This brought up new challenges that are related to not only etch controllability between silicon and silicon germanium, but also interface quality on SiGe channel.

In this presentation, we will discuss the etching challenge in the dual channel fin application. In the fabrication scheme, Si and SiGe need to be etched simultaneously, which requires etched rate controllability between the two materials. However, SiGe etch rate is higher than Si under halogen chemistries. In this investigation, we developed a novel plasma process that controls the etching characteristics (i.e., higher Si etch rate than SiGe) [2], leading to Si-SiGe etched amount control. We will reveal the etch mechanism of the plasma process utilizing surface analysis and ab-initio calculation.

In addition to the etch control, interface condition between gate oxide and SiGe channel is also critical. Sub-threshold can be improved by reducing interface trap density at the interface [3], which can be achieved by obtaining a Si-rich surface. There are a few conventional methods that can achieve a Si-rich surface on SiGe such as atomic layer deposition of Si cap over SiGe [4] and GeOx scavenging [5]. All of these require high temperature processes that cause issues such as atomic diffusion and strain relaxation. In this investigation, we will introduce a plasma treatment at room temperature that creates Si-rich surface. We investigated the mechanism of the surface modification into a Si-rich surface on SiGe under the plasma treatment [6]. We will also present how this has an impact on reducing interface trap density in terms of electrical performance.

[1]. O. Weber et. al., IEDM Tech. Dig., p.719, 2007

[2]. Y. Ishii et. al., Jpn. J. Appl. Phys. **57**, 06JC04 (2018)

[3]. C. H. Lee et. al., IEDM Tech. Dig., p.31.1.1., 2016

[4]. H. Mertens, et al., VLSI Tech. Dig., p.58, 2014

[5]. C.H. Lee, et. al., VLSI Tech. Dig., p. 36, 2016

[6]. Y. Ishii, et. al., IEEE J. Electron Devices Soc. **7**, 1277 (2019)

8:40am **PS-ThM-3 Investigation into the Effect of Plasma-Deposited $SiCl_4/O_2$ Chamber Wall Coatings on the Selective Fluorine-Based Etching of TaN with Respect to Polycrystalline Silicon and Silicon Oxide**, ***Ivo Otto IV,*** Tokyo Electron Ltd.; *C. Vallée,* SUNY Polytechnic Institute; *K. Yu, S. Kal, A. Mosden, P. Biolsi,* Tokyo Electron Ltd.

Tantalum nitride (TaN) is widely used as a crucial component of diffusion barriers within the back-end-of-the-line (BEOL) because of its strong dielectric adhesion and ability to scale low in-plane resistivity and diffusion-blocking capability to sub-5 nm thicknesses. In order to create the BEOL interconnect superstructure, a cyclical process of conductor and liner deposition and etching, followed by dielectric capping must be completed. In this paper, we will explore the use of inductively-coupled plasma (ICP) discharges containing NF_3/Ar, $NF_3/O_2/Ar$, and $NF_3/SiCl_4/Ar$ mixtures for the isotropic, dry etching of TaN; relying on radically-based etch, without non-selective ion bombardment. The aforementioned radically-based process is sensitive to chamber wall condition during the etching process; therefore, we considered that such methods often employ wall coatings in order to achieve superior etch uniformity and wafer-to-wafer reproducibility. This process is outlined in Figure 1; comparing the process utilizing coating and without utilizing coating. PATH A includes chamber conditioning without coating followed by the etching of the sample wafer, while PATH B includes the application of coating prior to sample wafer processing. The mechanism of $SiCl_4$ and O_2 PECVD of SiO_2 has been extensively studied, while the impact of the coating itself on metal and metal nitride etching has not been so well explored. The aforementioned dry-etching chemistries for the removal of TaN are compared with and without using a $SiCl_4/O_2$ chamber coating: comparing the etching process of the TaN film and etch selectivity to polycrystalline silicon and silicon dioxide. In-situ optical emission spectroscopy is utilized to find that the $SiCl_4/O_2$ chamber coating reacts with the ICP discharge to modify relative species densities when compared to a discharge without the chamber coating applied. Furthermore, modification does not only occur within the discharge, but at the film surface, where we use spectroscopic ellipsometry (SE) to find the etching selectivity of the TaN film is significantly changed with respect to the polycrystalline silicon and silicon oxide upon coating application. O_2 and $SiCl_4$ are separately added directly to the plasma discharge in order to characterize the effect of coating constituent gases and to ascertain if a similar affect to coating addition could be attained with direct addition of O_2 or $SiCl_4$ to the discharge. X-ray photoelectron ellipsometry is utilized in order corroborate SE findings, but to also give an idea of the fluorine-based etching pathway the TaN undergoes towards achieving full removal.

9:00am **PS-ThM-4 Influence of Aspect Ratio on Isotropic Etch Process: A Case Study with SiCN Material**, *P. Luan,* ***Andrew Nolan****, Y. Yoshida, Y. Han, P. Biolsi,* TEL Technology Center, America, LLC, USA; *K. Ken, N. Ikezawa,* Tokyo Electron Ltd., Japan

Etching of trenches and holes into low-k dielectrics is an indispensable process in very-large-scale integration (VLSI) applications. As the critical dimension (CD) size shrinks aggressively with the advancement of technology nodes, the same etch amount (EA) leads to significantly increased aspect ratio (AR, calculated by EA/CD). In this work, we use SiCN as an exemplary low-k dielectric to investigate the effect of AR in isotropic etch processes where F-containing neutrals are the dominant etchant and the effects from ions are minimized. Blanket SiCN films and Si shadow mask were used to form a testing structure with which AR ranging from 0:1 to 70:1 can be evaluated. The etch amount of SiCN materials and their refractive index were evaluated using Spectroscopic ellipsometry (SE). The surface composition pre- and post-etch processes were examined by X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) at various ARs. We found that the etch rate and surface composition inside the shadow mask are dramatically different from those outside, which reflects the effect of ions on SiCN etching. With higher AR, the etch rate of SiCN reduces whereas the surface composition of the etched SiCN film shows the formation of F-containing etch byproduct concentrated in the AR range between 15:1 and 45:1. The etch byproduct shows a characteristic XPS N1s peak at 403.8 eV, a Si2p peak at 105.1 eV, and a large amount of Fluorine. The accumulation such byproduct in this particular AR range could be resulted from the transport property of neutral-reactants from plasma and the lack of ion bombardment.

11:00am **PS-ThM-10 Plasma Etch Fundamentals and Engineering: Advancing Interconnect Scaling**, ***Theo Standaert,*** IBM Research Division, Albany, NY **INVITED**

Since IBM introduced Cu in 1997, the scaling of these interconnects has been relentless for more than two decades. Hundreds of miles of wiring are now deployed in a mindboggling small footprint for the most advanced computer chips, completing the electronic network for billions of transistors. Plasma etch has been and continues to be one of the essential process steps responsible for interconnect scaling. This review starts with some personal experiences as a young engineer, shortly after graduating in the field of plasma etch and surface science. Science and engineering are very different domains. Both are key for advancing and developing new technologies. In case of plasma etch engineering, one must understand the other processes and their constraints, both up- and down-stream in the manufacturing flow. Problems or challenges are rarely confined to a single process or sector. An example of isolated via etch-stop in a low-k dielectric will illustrate how very different engineering can be from science, and an interesting outlook for students and future engineers who are primarily focusing on science now. The review then continues through the past two decades, highlighting some of the key engineering innovations together with the plasma etch processes that enabled them, including patterning solutions for EUV and multi-layer. Finally, there are the future opportunities of interconnect scaling, arguably even more exciting than the past!

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[1] **2020 PSTD Young Investigator Award Winner**

11:40am **PS-ThM-12 Exploring the Use of Tungsten-Based Hard Masks in Beol Interconnects for 3 nm Node and Beyond***, **Daniel Montero**, V. Vega-Gonzalez, H. Puliyalil,* IMEC, Belgium*; J. Nie, J. Yang,* LAM Research*; F. Schleicher,* IMEC, Belgium*; K. Mclaughlin,* LAM Research*; J. Versluijs, F. Lazzarino, S. Park, Z. Tokei,* IMEC, Belgium

Scaling down the average chip size is one of the main drivers in the microelectronics industry, as it broadens the range of applications when smaller, cheaper, more efficient and more powerful chipsets can be installed in tighter packaging. However, scaling down does come with a price, the increased complexity during design and processing. An improvement from the stack composition point of view (materials and thicknesses) is needed, to keep up with the increasing demands while chip downscaling. Novel chip technology nodes require thinner patterning layers, to enable more advanced lithography steps (e.g., EUV lithography), which requires thinner photoresist layers, and therefore, thinner stacks, to transfer the pattern to the dielectric layers underneath [1]. It is in this context when robust and hard to etch materials (Hard Mask materials, HM), with higher etch selectivity are needed.

In the Back End Of Line (BEOL), TiN has been used as the HM of choice from many years in dual damascene applications [2]. As we approach to iN3 nodes and beyond, we face several issues while downscaling. The selectivity during dielectric etch may not be high enough to adequately transfer the pattern (line breaks, increased line roughness, loss of self-alignment during via patterning). TiN layer stress may not be suitable for tighter pitches, which may end up causing line wiggling. Another aspect is that fluorine-based chemistries, used to pattern the dielectrics below the HM, may form TiF salts, eventually leading to possible fail mechanisms.

Tungsten-containing layers have been proposed as viable candidates to replace TiN as HM in more advanced nodes. In this abstract, we first screen different W-containing layers deposited on blanket wafers, with varying W percentage content. Then, we demonstrate the etch development process of three different W-containing layers, acting as HM in line space patterning at tight pitches: at Metal Pitch 36 nm (MP36, line CD 18 nm), by means of an EUV single print lithography process, and at MP21 (line CD 10.5 nm), realized by means of ArFi lithography process and using a self-aligned quadruple patterning (SAQP) exercise. A first trench etch patterning exercise is done on SAQP P21 line space patterns to extract the average line roughness and HM selectivity values.

References

[1] D. de Simone et al, High-NA EUVL: the next major step in lithography. https://www.imec-int.com/en/articles/high-na-euvl-next-major-step-lithography

[2] H. Shi et al. Plasma processing of low-k dielectrics, chapter 3, ISBN 0470662549

12:00pm **PS-ThM-13 Reactive Ion Etch of Subtractive Metal for Advanced Interconnect***, **Lijuan Zou**, Y. Mignot, C. Penny, J. Arnold,* IBM Research Division, Albany, NY*; G. Stojakovic, P. Friddle, S. Schmitz,* Lam Research Corporation

The ability to etch metals in a controlled manner has potential applications at the forefront of advanced interconnect for semiconductor scaling. In this study, the authors evaluate Ru patterning and investigate in depth Reactive Ion Etching (RIE) mechanisms of Ru film in O2/Cl2/CH4 plasma. The etch rate; profile control and mask selectivity of Ru are examined as a function of Cl2/O2 gas ratio; passivation gas CH4 addition and bias power applied. By tuning polymerization, the authors achieve 90º Ru sidewall angle. The impact of various plasma parameters on structural and electrical performance are evaluated using a 300mm Transformer Coupled Plasma (TCP) RIE chamber. The plasma-material interaction is also studied with respect to masking materials. Each of these conditions are evaluated at aggressive critical dimensions to determine the impact of reduced feature size on the ability to anisotropically etch metal structures.

Plasma Science and Technology Division
Room 315 - Session PS-ThA

Harnessing the Power of Plasmas for Real-World Applications: PSTD Award Lectures

Moderators: Sebastian Engelmann, IBM T. J. Watson Research Center, **Mingmei Wang**, Lam Research Corporation

2:20pm **PS-ThA-1** ***Time-Resolved Energy and Ion Energy Distributions during High-Powered Impulse Magnetron Sputtering (HIPIMS) with Cathode Voltage Reversal* , *David Ruzic*[1]**, University of Illinois*; D. Barlaz, Z. Jeckell,* University of Illinois at Urbana-Champaign*; W. Huber, I. Haehnlein,* University of Illinois at Urbana-Champaign, Starfire Industries LLC*; T. Houlihan, B. Jurczyk,* Starfire Industries LLC **INVITED**

Reversing the potential on the cathode sputtering target immediately after the negative voltage pulse does remarkable things to the plasma, and if controlled correctly can make vastly superior thin films for a variety of applications.HIPIMS works by making a plasma dense enough to ionize the material being sputtered.Those target ions mostly return to the target and do self-sputtering.This leads to a very high current which is why the process is pulsed. Its advantages are that a small number of these ions do escape and go to the substrate, resulting in a higher ionization fraction.Its disadvantage is that fewer total atoms or ions reach the substrate resulting in a lower deposition rate.

Adding a positive voltage to the target changes everything.The plasma is expelled form the target region filling the device all the way up to the substrate being coated.This wave of plasma causes additional ionizations of the sputtered material, therefore increasing the ionization fraction reaching the substrate an increasing the deposition rate.The key though is that the plasma potential is raised by the exact voltage value of the positive pulse.This means that the ion energy reaching the substrate is controllable, without having to bias the substrate.In addition, by varying the time duration of the positive pulse with respect to the negative pulse, the ratio of target ions to working gas (Ar) ions can be controlled as well.

This talk will show detailed measurements of how this all occurs as a function of time including fast camera images.Several examples highlighting the applications made possible by such a system will be shown as well.

3:00pm **PS-ThA-3 PSTD Plasma Prize Award Talk: Plasma ON then OFF, ON - OFF, ON – OFF, ON - OFF: Who Knew Being Indecisive Could Work So Well!*, Lawrence Overzet*[2]*,*** University of Texas at Dallas **INVITED**

The reasons for modulating the power to a plasma can seem obvious at first. Shorter on time durations can enable one to operate at much higher instantaneous powers! One could potentially reach a power regime which is not sustainable for the same system in continuous wave (CW). In fact, one of the early papers on modulating the power to an RF plasma did so because the plasma system couldn't handle the CW heat load;[1] but then the researchers discovered something quite surprising! We tend to assume that the electron density grows as the power increases during the plasma turn-on in a somewhat “quasi-equilibrated” fashion. Further, most of us have assumed (at one point or another) that the plasma is just decaying toward zero during the off times. Slow neutral chemistry is occurring and some ion-molecule reactions too of course, but nothing all that particularly interesting or worthwhile. Even though all the above seems clear to a great majority of us, it turns out that it can be downright wrong. I've spent the greater portion of my career studying the kinetics and mechanics of how plasmas turn on and then off (and back on again) because I find those kinetics to be fascinating. (I also feel a need to state that making those measurements and models can be quite challenging!) I've found that the fashion in which energy is put into the plasma's electron population varies in time during the turn-on and turn-off. The chemical reactions can change in surprising fashions because of this and few things are as simple as one might expect. Particles confined by a CW plasma can suddenly be encouraged to leave, electron densities can increase as the power to the plasma decreases, fewer electrons can cause more reactions (and light) and plasma diagnostics can be enabled which otherwise might not even be imagined.

[1]R. Boswell and D. Henry, Appl. Phys. Lett. 47 (10) 1095-7 (1985).

3:40pm **PS-ThA-5 PSTD Young Investigator Award Talk: Next Generation “Birkeland-Eyde”: From NH_3 to NO*, Floran Peeters*[3]*,*** DIFFER, Netherlands **INVITED**

In 1905 industrial-scale production of nitric acid began in Notodden, Norway. This development came in response to a global shortage of nitrogen fertilizer, required to feed the world. Where for years nitrogen fertilizer was obtained by harvesting diminishing supplies of guano, several initiatives were undertaken to produce nitrogen fertilizer artificially. Scientists and engineers in the US and in Europe independently developed nitrogen fixation methods based on breaking the strong molecular nitrogen bond using electric arcs, forming NO as an intermediate chemical. Sustaining arc discharges continuously, a definite requirement for commercial exploitation, leads to electrode sputtering and thus a limited lifetime of the reactor. This problem was solved by Birkeland and Eyde by rotating the arcs in a magnetic field, leading to a 40 MW nitrogen fixation plant which remained operational until the 1920's.

Starting in the 1910's the use of electric arcs for the fixation of nitrogen was slowly overtaken by the more energy-efficient catalytic Haber-Bosch process, in which NH_3 is formed from atmospheric nitrogen and hydrogen from natural gas. This high temperature, high pressure process, while an engineering marvel in its own right, suffers from a major drawback when viewed through a modern lens: its heavy reliance on fossil fuels.

With the global aim of transforming the chemical industry to rely on sustainably generated electricity,interest in fixing atmospheric nitrogen using only electrical power has gained renewed interest. In this contribution, an analysis will be given of the existing nitrogen fixation production chains and the possibilities and benefits of replacing these with new, plasma-based methods. Using insights gained from over a century of scientific literature, recent experiments and models, strategies for improving plasma-based nitrogen fixation methods will also be discussed.

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[1] **2020 AVS Gaede-Langmuir Awardee**

[2] **2021 PSTD Plasma Prize Winner**

[3] **2021 PSTD Young Investigator Awardee**

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

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[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.

Plasma Science and Technology Division
Room 315 - Session PS2+SE-FrM

Plasma Sources, Diagnostics, Sensors and Control
Moderator: Nathan Marchack, IBM T.J. Watson Research Center

8:20am **PS2+SE-FrM-1 Optical and Electrical Diagnostics of Industrial Plasma Reactors: Measuring the Relevant Physical Quantities to Assist Process Development*, Gilles Cunge*,** LTM/CNRS-UJF, France*; S. Younesni,* STMicroelectronics/CNRS-LTM France*; N. Loubet, M. Kogelschatz, E. Pargon, C. Petit-Etienne, O. Joubert, E. Despiau-Pujo, N. Sadeghi,* CNRS-LTM, Université Grenoble Alpes, France **INVITED**

As new devices with 3D architectures and new materials are introduced in the microelectronic industry, plasma etching processes are more and more challenged. The necessity to pattern nanometer size features (with high aspect ratio) with an ultrahigh selectivity towards underlayers has pushed the development of new plasma processes with advanced RF power and/or gas injection pulsing schemes. The goal is either to achieve atomic layer etching processes or simply to overcome typical plasma limitations (charging effects, ARDE…etc). However, since the number of different processes possible in a reactor increases rapidly with each new control knob, the development of innovative processes is becoming extremely difficult with empirical approaches (i.e. DOE). It is thus mandatory to get a deep understanding of the impact of knew control knobs on the plasma properties to develop such new processes efficiently, which can only be achieved by using plasma and surface diagnostics. In this paper, we will review plasma diagnostics that are the best adapted to get a clear picture of the impact of the reactor control knobs on the process performances. Plasma diagnostics are separated in two categories: 1) those used to detect radicals (etchants or etch products) with a time resolution of about 1 ms, i.e. modulated beam mass spectrometry as well as spectroscopic techniques such as optical emission spectroscopy, absorption spectroscopy (from the VUV to near IR range) and Laser induced fluorescence. 2) techniques used to measure the charged species with a µs time resolution: specific Langmuir probe for the ion flux measurements in aggressive environment, RFEA for ion energy distribution function and mass spectrometry/RFEA to analyses the ion nature. We will show that it is important to couple plasma diagnostics with surface analysis (e.g. XPS, Raman…etc) to get a clear picture of the mechanisms involved in new processes and illustrate this point with several concrete processes developments in industrial reactors (ranging from pulsed ICP plasmas to downstream processes).

9:00am **PS2+SE-FrM-3 Hole Transport Properties of Nickel Oxide Films Grown via Hollow-Cathode Plasma-Assisted Atomic Layer Deposition***, S. Ilhom, A. Mohammad, M. Niemiec, D. Zacharzewski, P. Chardavoyne, S. Abdari,* ***Necmi Biyikli,*** University of Connecticut

In contrast to the relative abundance of as-grown unintentionally doped n-type semiconductor materials, there are only a few alternative alloys showing p-type conduction without needing extra high-temperature doping processes. NiO is of particular interest mainly due to its stability and promising performance as hole-transport layers in emerging solar cell device structures. However, to broaden the NiO application domain towards potential back-end-of-the-line (BEOL) transistor devices as potential p-type channel layers, the transport properties of NiO needs to be improved significantly. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in p-type NiO films with atomic-level precision and large-area uniformity, the hole mobility is far from being sufficient, typically lower than 1 cm^2/Vs.

In this study we have carried out a systematic study on plasma-enhanced ALD (PEALD) of NiO films on Si and glass substrates using nickelocene ($NiCp_2$) and O_2/Ar plasma mixture using hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD). Detailed saturation studies using in-situ ellipsometer monitoring were carried out in the HCP-ALD reactor, scanning for $NiCp_2$ pulse time, O_2 plasma exposure time, purge time, and plasma power. Optimal growth conditions were identified as 90 ms $NiCp_2$ pulse / 5 s purge / 10 s O_2-plasma at 100 W plasma exposure / 5 s purge. 800 cycle runs were conducted to evaluate the substrate temperature impact (100 - 250 °C) on growth-per-cycle (GPC) and film properties.

The resulting p-type NiO films are characterized for their structural, optical, and electrical properties. Films grown at optimal conditions (200 °C) exhibit refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on both Si and glass substrates exhibit polycrystalline single-phase cubic structure (*c*-NiO). In order to determine the carrier type and extract field-effect mobility values, we have fabricated vertical NiO/n-Si p-n junction diodes as well as NiO/Al_2O_3/Si thin-film-transistor (TFT) device prototypes to characterize diode I-V behavior and confirm p-type layer structure for NiO, and extract the field-effect carrier mobility, respectively. Our I-V measurement results confirmed p-n junction diode characteristics with decent ON/OFF ratios for forward and reverse diode current values. TFT characterization results as well as detailed temperature-dependent Hall measurements will be used to identify critical hole transport parameters.

9:20am **PS2+SE-FrM-4 In-Situ Measurement of Electron Emission Yield at Silicon Surfaces in Ar/CF4 Plasmas*, Mark Sobolewski,*** NIST

Plasma simulations require accurate data for the ion-induced electron emission yield at plasma-exposed surfaces. For industrially relevant plasmas, however, direct measurement of yields using ion beams is impractical. In contrast, measurements made in situ, during plasma exposure, provide useful values for the total or effective yield produced by all incident ions. Here, in-situ measurements were performed in an icp system in Ar/CF4 mixtures at 1.3 Pa. The current and voltage across the sheath adjacent to the rf-biased substrate electrode were measured, along with Langmuir probe measurements of ion current density and electron temperature. The measurements are input into a numerical sheath model, which allows the emitted electron current to be distinguished from other currents. The effective yield was determined for thermally oxidized, in-situ etched, and sputter-cleaned silicon surfaces. For thermal oxides in pure Ar, yields agreed with previous measurements [1] on sputtered oxides. By combining measurements made for several mixtures with mass spectrometer data for the relative flux of each ionic species, estimates or bounds were obtained for the individual electron emission yields of the most prevalent ions. [1] M. A. Sobolewski, Plasma Sources Sci. Technol. 30 025004 (2021).

9:40am **PS2+SE-FrM-5 Plasma Characterization: Radical Recombination Sensor Based on Dual Probe Thermopile Heat Flux Sensors*, Johannes Velthuis,*** TNO Science and Industry, the Netherlands

Hydrogen radicals play an important role in e.g. the cleaning of EUV reflective mirrors. Therefore there is the need to quantify the surface radical flux in the various (plasma) setups where these effects are studied. In this paper a catalytic radical sensor is presented, based on the measurement of the recombination heat of radicals on a surface, using dual probe thermopile Heat Flux Sensors (HFS). The first HFS1 has a high recombination (probability) coefficient coating, e.g. Pt. The second HFS2 has a low recombination coefficient coating, e.g. Al2O3. Signal subtraction largely eliminates common mode heat losses/gains such as conduction/convection and IR-radiation, the net result representing the radical recombination heat. The signal can be improved by switching the radical source on/off at regular intervals. Radical recombination rates where measured in a remote microwave (MW) plasma chamber (38 Pa H2) over the range 1E18−1E21 atH/(m2s), with nearly linear response as function of plasma power setting. The sensor full scale limit is ~1E23 atH/(m2s) and is dictated by the maximum allowable sensor surface temperature (<250oC).

10:00am **PS2+SE-FrM-6 Dielectric Toroidal Plasma Sources for Improved Plasma Resistance*, Ilya Pokidov,*** MKS Instruments

A new sintered alumina toroidal plasma source has been developed that overcomes the limitations that a quartz or hard anodized coated aluminum alloy applicator have. This alumina ceramic applicator is implemented in R*evolution® toroidal remote plasma source (RPS) chassis replacing the quartz, which predominantly is used in photoresist strip by oxygen plasma. The toroidal body is made of 99.5% pure alumina, more resistant than quartz to harsh plasma chemistries, such as H, F and Cl. It can withstand higher ignition and operating voltages, allowing to ignite plasma directly in process gas. Ceramic alumina is a very pure material. Impurities are below 0.5% versus the hard anodized coating typically grown from the base 6061 alloy with impurity content of up to 4.2%. The ceramic extends the principal limitation of quartz in handling halogen and hydrogen plasmas.

The torus is fabricated by first machining two identical halves in green state and then co-firing them together to form a high strength hermetic bond. Afterwards, the alumina torus' exterior surface is surrounded by a potting compound with high thermal conductivity and low elastic modulus and encapsulated inside a copper cooling jacket to minimize thermo-mechanical stress on the ceramic.

Tests of the alumina ceramic applicator indicate that it can safely operate up to 6kW, full range of R*evolution RPS power without fracturing. Plasma successfully ignited in process gases such as O_2/N_2, H_2, and N_2/H_2 with healthy operating windows. The alumina applicator underwent a 1000-hour life test in forming gas plasma without significant signs of surface erosion. Similar construction methodology is applicable to sapphire. However, a prototype sapphire torus has shown a lower operating power range than the alumina torus.

The paper will present the design methodology to address key technical challenges in the development of a dielectric toroidal applicator for a transformer coupled remote plasma source. Test data will also be presented to demonstrate operating windows and radical output capabilities of the ceramic toroidal remote plasma source in different gas chemistries.

10:20am **PS2+SE-FrM-7 What We Still Won't Know About Plasmas in Simple Diatomic Gases- or Using a DC Glow Discharge in Pure O_2 as an Ideal Test-Bed for Experimental Validation of Models*, Jean-Paul Booth*[1]*,*** LPP-CNRS, France **INVITED**

Despite many decades of study, models of discharges in molecular gases still lack accurate data on many key collisional processes, even for such "simple" and ubiquitous gases as O_2. Good data is lacking for near-threshold electron-impact dissociation with neutral products, the role of metastables; of gas heating, vibrational excitation and energy transfer processes; as well as surface recombination and thermal accommodation. Direct measurement of the rate constants of individual processes is a fastidious process, where it is even possible. As an alternative approach, we compare comprehensive measurements of internal plasma parameters to simulations for a plasma with relatively simple chemistry, namely a DC positive column discharge in pure O_2. This well-characterized, stable and uniform discharge is optimal for experiment-model comparison. Although this system has been studied for a many decades, new experimental methods, including synchrotron Vacuum ultraviolet absorption spectroscopy and laser cavity ringdown absorption spectroscopy (CRDS), allow the densities of all the major species (atomic, molecular, in ground and excited states) to be measured, with much-improved absolute accuracy, and with time resolution. The gas translational temperature, and vibrational energy distribution, were also probed. Applied to (partially- and fully-) modulated discharges, these measurements provide unprecedented insight into the kinetic processes occurring, and a profound test of the models. Whereas models can be quite easily adjusted to fit steady state measurements at one given set of operating conditions, trends with pressure and discharge current, and especially the temporal response to current modulation, are much harder to reconcile. In practice, model failures can often be attributed to simple omission of key processes, or to the neglect of their temperature-dependence. If the chemistry studied is simple enough, and the measurements cover all of the principal species (stable molecules in their ground and metastable states, atoms and negative ions) as well as the gas temperature, it becomes possible to identify the missing reactions, and even estimate their rates and activation energies, by adjusting their values in the model to fit the observations. As examples, we have demonstrated that the kinetics of metastable O_2 b molecules cannot be modelled without the inclusion of quenching by oxygen atoms with a significant activation energy. We have also demonstrated the production of ozone by the reaction of O_2 molecules with oxygen atoms chemisorbed on the glass discharge tube walls.

11:00am **PS2+SE-FrM-9 Voltage and Sheath Dynamics in Electropositive Capacitively Coupled Plasmas with Focus Ring and External Circuit*, Yuhua Xiao*,** *J. Brandon, J. Morsell,* NCSU*; S. Nam, J. Lee,* Samsung Electronics Co., Inc., Republic of Korea*; S. Shannon,* NCSU

Capacitively coupled plasmas (CCPs) are widely used in semiconductor processes. The control of plasma to obtain uniform deposition and etching over a large process space is still an open problem, particularly within a few millimeters of the substrate edge. Complex material stacks commonly referred to as focus rings (FR) or process kits are placed at the wafer edge to balance process non-uniformities and provide uniform process to the edge of the substrate. This solution has limitations with regard to process window and eventual material erosion.One promising approach is to combine a focus ring assembly with a tunable external circuit (EC) ground path termination to extend the plasma uniformity to the wafer edge over a wider process space. The effect of FR combined with EC for fine adjustment and minimization of edge process area are presented here. In this work, a simplified FR with EC structure consisting of a variable capacitor and an inductor is adopted to change the impedance between electrodes and the

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[1] **2019 PSTD Plasma Prize Winner**

ground, and the sheath voltage distributions and width are modified. Experimental results are measured using hairpin probe, high-voltage RF and DC probes, in-line RF metrology at the powered electrode, and intensified CCD camera imaging of the electrode edge and FR region. The results are further compared to simulations, which use an equivalent circuit model to simulate the effect of this structure on sheath properties. Results show that the FR with EC structure can partially control the DC self-bias and distribute the voltage and the energy loss among different sheaths associated with different electrodes. The EC can affect the sheath dynamics and equipotential lines of the center and near the wafer edge prominently. These results point to possible source design based pathways for engineering the distribution of power dissipation across these sheaths in industrial plasma reactors to improve process performance at the electrode edge.

11:20am **PS2+SE-FrM-10 Time Resolved Diagnostics of a Silver HiPIMS Discharge***, **Zachary Jeckell**, D. Barlaz, R. Ganesan, D. Kapelyan, K. Martin,* University of Illinois at Urbana Champaign*; W. Huber, B. Jurczyk,* Starfire Industries LLC*; D. Ruzic,* University of Illinois at Urbana Champaign

This work aims to investigate the temporal evolution of a high-power impulse magnetron sputtering (HiPIMS), with a positive cathode reversal, discharge by using the Hiden ANALYTICAL PSM probe, that can measure the ion energies as well as perform charge to mass (q/m) measurements. This allows for time resolved differentiation between the working gas and the sputtered material, which in this case is silver, and enables the quantification of the population of ions at higher charge states. Q/m differentiation allows for the construction of Ag^+/Ar^+, which when combined with previous IEDF measurements can help tailor future depositions to maximize the flux of silver ions. Our previous work studying the time evolution of the IEDF showed the peak energy of the distribution shifts to the set positive pulse voltage within 3 us regardless of conditions, and that there is a clear difference in the distribution during the first 20 us of the cathode reversal and the end of the cathode reversal, which we attributed to a higher presence of metal ions that are ionized in flight. This work would aim to verify this claim as well as quantify the population of silver in higher charge states. Investigating the population of Ag^{2+}, and other higher level charge states, is of interest because it is believed to lead to film damage for cases of large positive pulse biases, as the energy of the ions will likely be in the etching regime on the HiPIMS structural zone diagram. Multi-ionization results will be compared with fast camera measurements to see if the population of higher order charged states are correlated to the presence of hot spots. The fast camera measurements are taken using the PI-MAX 4 camera with a selected gate width of 100 ns. Additionally, the ionization fraction of silver can be found and the correlation between measured ionization fraction and the deposition rate measured with a quartz crystal microbalance (QCM) can help to determine the fraction of ions that return to the target and self-sputter as well as the fraction of ions that are transported to the substrate.

11:40am **PS2+SE-FrM-11 Title: Curling Probe Analysis for Practical Measurement of Electron Density***, **Daisuke Ogawa**, K. Nakamura, H. Sugai,* Chubu University, Japan

Optical monitoring is a powerful diagnostic tool for plasma processing, but it should be reminded that optical emission from plasma is still secondary information.As learned from a plasma textbook, photon emission results from many electron relaxations of excited species.Behind the relaxation processes, electrons play a role in transferring their energy to create the excited species. The reaction rate of such reactive species strongly depends on electron density and temperature.Therefore, electron monitoring can be a powerful processing diagnostic even in a practical plasma because electron information can be utilized to know radiative and non-radiative species.Aiming for practical use of electron diagnostic, we have developed a curling probe, one of the diagnostics for finding electron density in plasma with a microwave-range electrical resonance.Plasma has a smaller dielectric constant than vacuum, making resonant frequency smaller. The degree of the frequency shift indicates electron density in plasma. The curling probe utilizes the measurement principle, and in particular, the probe utilizes a slot antenna to obtain the resonance.Due to the regulation of the probe space, the antenna is spiral-shaped and configured in a plane.So, the antenna configuration has some unique characteristics, which are not found in other microwave resonating probes, such as a hairpin probe. One of the unique characteristics of the probe is that the probe has a directionality of electron density measurement.We currently consider that the probe enables us to include the probe into an electrode.This configuration is possibly applied to a narrow-gaped capacitively coupled plasma. Our former work showed that the probe is getting ready for practical use because the probe operates under film depositing situations (Ogawa et al., PSST 30 (2021) 085009) with high pressure (<1000Pa). However, the probe still needs to be improved because we have noticed that the probe temperature affects the degree of the resonant frequency shift.We recently measured and analyzed the probe temperature and degree of resonant frequency shift, and found that the resonant frequency shift has a regularity in temperature. The regularity successfully enabled us to calibrate the probe measurement and showed that the probe is ready to utilize temperature-varying situations.This presentation will show our recent progress in electron density measurement with a curing probe under the temperature-varying situation.This presentation will provide an opportunity to discuss how to apply the probe to an industry reactor.

Advanced Surface Engineering Division
Room 317 - Session SE+MN+PS-FrM

Nanostructured and Multifunctional Thin Films and Coatings II

Moderators: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan , **Filippo Mangolini**, The University of Texas at Austin

8:20am **SE+MN+PS-FrM-1 New Challenges and Opportunities for Hard and Superhard Coatings***, **Aharon Inspektor**,* Carnegie Mellon University**INVITED**

Many hard, superhard and lubricious coatings with superior mechanical properties, thermal stability and chemical resistance are being developed and applied for surface protection in harsh and demanding applications. In this paper we will discuss the status and foreseen trends in PVD hard, superhard and lubricious films.

First, we will review the design of current multifunctional hard coatings and their applications in metal cutting, in automotive and in aerospace industries. Next, we will examine how the Forth Industrial Revolution, a multi-level connectivity of sensors and systems, with “Smart Manufacturing”, computer controlled automated facility system, will affect future usage of multifunctional coatings. The talk will conclude with a critical discussion of the resultant challenges and opportunities for next generation of hard, superhard and lubricious coatings.

Thin Films Division
Room 316 - Session TF1+PS-FrM

Plasma, PVD and HIPIMS Processes for Emerging and Advanced Materials

Moderators: Joe Becker, Kurt J. Lesker Company, **Christophe Vallee**, SUNY College of Nanoscale Science and Engineering

8:40am **TF1+PS-FrM-2 Growth of c-axis Textured AlN PVD Film on a 2D-MoS_2 Seed Layer***, **Julien Patouillard**,* STMicroelectronics, France*; E. Blanquet, A. Mantoux,* SIMaP, CNRS, University Grenoble Alpes, France*; F. Gianesello,* STMicroelectronics, France*; M. Bernard, S. Cadot, R. Gassilloud, C. Raynaud,* Commissariat à L'énergie Atomique, France

Aluminum nitride (AlN) is a piezoelectric and wide bang gap material which crystallizes in a hexagonal wurtzite structure. This material arouses a certain interest in various fields of microelectronics, in particular radiofrequency (RF) devices [1–3]. Its deposition process is well-known and appears to be reproducible, using either epi-like chemical deposition solutions, or N_2-based physical deposition with Al-target. In particular, AlN deposited by Physical Vapor Deposition (PVD) exhibits a relatively large electromechanical coupling coefficient $k_t^2 \approx 6{,}5\%$. [2]

Due to the lack of bulk AlN substrates and the large lattice mismatch between AlN and silicon, AlN is usually epitaxially grown on sapphire or silicon carbide (SiC) substrates at high growth temperature (≈1000 °C) to achieve higher crystalline quality and hence better device performance [4,5]. However, high cost, limited wafer size or differences in thermal expansion coefficient between AlN and these substrates drastically limit the integration and applications of AlN.

In recent years, the emergence of 2-Dimensional (2D) materials and particularly 2D-Transition Metal Dichalcogenides (2D-TMDs) seems to be a promising approach for the growth of III-nitride. Among 2D-TMDs, MoS_2 is one of the most widely studied materials due to its availability [6,7]. MoS_2 has a natural two-dimensional structure with the sandwich-like S-Mo-S layers serving as building blocks, in which the atoms in the layer are bonded with strong covalent bonding, while the layers are packed together with weak interlayer forces [8,9]. It also presents a hexagonal structure with a close lattice matching with III-nitride (1 % to 3 %) and a chemical compatibility enabling the direct growth of these materials [4,5].

In this presentation, we will demonstrate the direct growth of c-axis textured AlN films deposited by PVD on a well-controlled and uniform MoS_2thin film elaborated by Atomic Layer Deposition (ALD). We will show how 2D materials can be advantageously implemented to improve the texturation of AlN on silicon substrate. Hence, in figure 1, the crystal quality of AlN is assessed by X-Ray Diffraction (XRD) measurements using the Rocking Curve (RC) technique. The FWMH of the omega peak at 18° (Theta 36,04° of (002)) gives a direct information on the mosaicity of the AlN layer. AlN Growth on 2D-MoS_2 seed induces a strong reduction of FWMH compared to Si-based substrate, indicating the preferential reorientation of the AlN matrix along the (002) axis, perpendicular to the substrate surface. This orientation is expected to boost the piezoelectric coefficient, which opens new field of applications on Si substrate.

9:00am **TF1+PS-FrM-3 Synthesis and Hardness of Thin-Film High-Entropy Transition Metal Ceramics*, Nathaniel McIlwaine,*** The Pennsylvania State University*; M. Hossain,* Pacific Northwest National Lab*; J. Maria,* The Pennsylvania State University

High entropy carbides (HECs) are single phase, multicomponent materials that possess a high degree of configurational entropy on cation lattice sites and can possess enhanced thermal and mechanical properties compared to binary transition metal carbides. Group IIIB, IVB, VB, and VIB transition metal HECs with high hardness and high melting temperatures are prospective materials for refractory applications such as advanced armor, cutting tools, and spacecraft thermal protection systems.

HECs are chemically disordered crystals containing components inclined to form ternary solid solution compounds and carbon deficient phases. Multicomponent carbides produced by conventional reactive sputtering techniques, such as radio frequency (RF) and direct current (DC), are hindered in overall film quality due to uncontrolled microstructure and stoichiometry. This work is focused on the synthesis of HECs through reactive bipolar high-power impulse magnetron sputtering (HiPIMS) to overcome these conventional challenges.

Through HiPIMS, HEC crystals structurally and compositionally transform as a function of the carbon to metal ratio (C/M), providing access to metallic, ceramic, and composite carbides. By increasing the methane flow rate during sputtering, this introduces a carbon-deficient metallic (C/M < 1), transitions to a stoichiometric ceramic zone (C/M ~ 1), and finally culminate in an excess-carbon, nanocomposite regime (C/M > 1) at high methane flow rates. Combinations of X-ray diffraction, Raman spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and nanoindentation/microindentation hardness measurements form these three zones. Achieving the stoichiometric ceramic zone is of particular interest to maximize the hardness of a given HEC composition. HiPIMS is able to produce HECs with ceramic zones over a larger range of methane flow rates than RF or DC sputtering.

9:20am **TF1+PS-FrM-4 Structural Evolution and Thermoelectric Properties of Flexible Mg_2Sn Films Prepared by Magnetron Co-sputtering*, Sara Kim,*** *S. Kang, N. Kim,* Chosun University, Republic of Korea

Thermoelectric (TE) materials are capable of harvesting waste heat and converting it into useful electrical power which contributes significantly to improved energy efficiency. Recently, the development of flexible TE materials and devices has become a significant focus in the thermoelectric field due to the need for wearable and autonomous devices. The flexible TE materials can effectively harvest waste-heat from hot surfaces in a wide temperature range for applying to power generation in industry and human life. The anti-fluorite Mg_2X (X = Si, Ge, Sn)compounds have attracted great attention owing totheir non-toxicity, low manufacturing cost, light weight, and flexibility [1]. In this study, several un-doped Mg-Sn films were deposited onto polyimide substrates by radio frequency magnetron co-sputtering with Mg and Sn targets. Mg sputtering power was fixed while Sn sputtering power was varied to prepare Mg-Sn films with different stoichiometry. Then, Mg and Sn sputtering time was varied to prepare films with different thicknesses while the sputtering power was fixed. The TE performances as well as the flexibilityof the samples were analyzed in terms of point defects and structural evolution of the samples during flexibility test. Folding tests with different folding cycles were carried out for flexibility evaluation of the samples. The structural properties, chemical composition, and Hall characteristics of the Mg-Sn thin films before and after the folding test were analyzed using X-ray diffraction, energy dispersive X-ray spectroscopy, and Hall effect measurement system, respectively. The electrical resistivity and Seebeck coefficient as a function of temperature were simultaneously measured up to 703 K. Acknowledgement: This work was supported by the Gwangju·Jeonnam Local Energy Cluster Manpower Training of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy (No. 20214000000560). [1] J. I. Tani, and H. Ishikawa, Thin Solid Films 692, 137601 (2019).

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