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.

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

Advancing Metrology and Characterization to Enable Atomic Scale Processing

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

By scattering noble gas ions from the surface of the sample, LEIS determines the elemental composition of the surface of the outermost atomic layer. Nucleation processes and layer closure are investigated, but also diffusion from the bulk towards the surface can be studied with in-situ sample heating and continuous monitoring of the surface composition.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Nanoscale Science and Technology Division
Room 304 - Session NS2+AP+BI-MoA

Fabrication and Operation of Nano-Systems

Moderator: David Czaplewski, Argonne National Laboratory

4:00pm **NS2+AP+BI-MoA-8 Control of Color Centers in Diamond using Photonic and Phononic Crystals***, **Kazuhiro Kuruma**,* Harvard University **INVITED**

Color centers in diamond are one of the promising solid-state quantum emitters for the realization of on-chip quantum network. In particular, SiV centers have been investigated owing to their optically accessible spins as well as large and stable zero phonon line emission in photonic nanostructures. The integration of the SiV centers into the nanostructures such as photonic crystal nanocavities has been demonstrated as an efficient spin-photon interface for various quantum applications [1]. However, SiV centers need operations at mK temperatures [2] or under static strain [3] to achieve a long spin coherence time. I will show another potential approach using phononic crystals as a way to enable the realization of a long spin coherence time at higher temperatures[4]. Our efforts aimed at efficient control of the SiV spins using diamond optomechanical cavities will also be discussed [5]. Finally, I will present our works on the integration of tin-vacancy (SnV) centers, alternatives to SiV centers for operations at higher temperatures, into free-standing photonic crystal nanocavities [6].

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4:40pm **NS2+AP+BI-MoA-10 Scalable Preparation of Intrinsically Chiral Metal Surfaces for Enantioselective Processes***, **Nisha Shukla**, A. Gellman,* Carnegie Mellon University, USA

Chiral surfaces are critical components of enantioselective heterogeneous processes such as those used to prepare enantiomerically pure pharmaceuticals. While the majority of chiral surfaces in practical use are based on achiral materials whose surfaces have been modified with enantiomerically pure chiral adsorbates, there are many inorganic materials with valuable surface properties that could be rendered enantiospecific, if their surfaces were intrinsically chiral.

This work discusses recent developments in the fabrication of intrinsically chiral surfaces exhibiting enantiospecific adsorption, surface chemistry and electron emission. We propose possible paths to the scalable fabrication of high-surface-area, enantiomerically pure surfaces and discuss opportunities for future progress.

5:00pm **NS2+AP+BI-MoA-11 Wrinkle-Induced, Scale-Dependent Mechanical Properties in Nanometer Thick Films***, **Jian Zhou**, N. Moldovan, L. Stan, J. Wen, D. Jin,* Argonne National Lab*; D. Lopez,* Pennsylvania State University*; D. Czaplewski,* Argonne National Lab

Micro- and nano-electromechanical (MEMS/NEMS) devices have relied heavily on materials typically used in electronic devices. The majority of MEMS/NEMS devices are fabricated with a top-down approach to take advantage of the corresponding highly reproducible fabrication processes associated with silicon related materials. As a natural extension, as devices move into the nanoscale regime, new materials are introduced using the same fabrication paradigms used for electronics: ultra-flat surfaces, controlled stresses, simply defined materials properties, with precision 2-dimensional or 2+ dimensional definition using lithographic techniques. New materials, such as 2D materials, began to be incorporated with great promise. However, creating 2D material films that behave like traditional silicon-related films has become challenging due to their unconventional growth/deposition techniques. A typical method for depositing a 2D film is through a transfer process, which struggles to create flat, low stress, thin films. This has led to films that have variations in properties, as observed in large deviations in values reported for parameters such as Young's modulus.

In this work, we explore the variation in properties of films as they become more 2+dimensional textured versus being ultra-flat. We measure the response of resonators fabricated from both ultra-flat and wrinkled films. The ultra-flat films follow expected behaviors with small deviations in resonant frequency and bending rigidity. However, the wrinkled films have a frequency response that is highly variable, up to 45 times that found in flat films. Additionally, we find that the increased rigidity and distribution of values is scale-dependent. As we vary the in-plane dimensions of the resonant structures, we find that the characteristic values scale with the structure dimension. This matches very well with a theoretical model proposed to describe thermal fluctuations in thin films. This opens a new paradigm for device design that allows a single film to have multiple elastic properties based solely on the patterning size. Going forward, we see this being an interesting tool in the design of devices made from single nanometer-thick films.

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.

References

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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 ($115 nm < \lambda < 180 nm$) 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.

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].

[1] J.C. Gertsch et al., “Deposit and Etchback Approach for Ultrathin Al_2O_3 Films with Low Pinhole Density Using Atomic Layer Deposition and Atomic Layer Etching”, *J. Vac. Sci. Technol. A***39**, 062602 (2021).

[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).

Atomic Scale Processing Focus Topic
Room Ballroom A - Session AP-TuP

Atomic Scale Processing Poster Session

AP-TuP-1 A Computational and Experimental Investigation of Platinum Vapor Deposition Reactions on Oxygen and Nitrogen Functionalized Carbon*, I. Campbell, N. Nayir,* Penn State University*; S. Kuespert, N. Ortlieb, A. Fischer,* University of Freiburg, Germany*; A. Van Duin, **Suzanne Mohney**,* Penn State University

Nitrogen-doped carbons are useful as supports for catalysts due to their low cost, low density, and enhanced metal-support interaction. We used density functional theory (DFT) to evaluate the effects of N-doping and oxidation of graphene on the adsorption and dissociation of trimethyl (methylcyclopentadienyl) platinum ($MeCpPtMe_3$), which is commonly used for synthesizing platinum nanoparticles and films by chemical vapor or atomic layer deposition. We confirmed that oxygen incorporation in graphene via oxidation of monovacancies is thermodynamically favorable with and without N doping and discovered that N doping elongates substrate-oxygen bonds, indicating increased reactivity of the oxygen atoms bound to the substrate. According to nudged elastic band calculations, the transfer of a Me ligand from $MeCpPtMe_3$ to oxidized substrates with and without N-doping displays positive enthalpies of reaction and activation energies, making Me transfer a rate determining step. However, nitrogen doping thermodynamically and kinetically drives the Me dissociation reactions by lowering the enthalpies and activation energies of the reactions. We also showed that the dissociation of $MeCpPtMe_3$ and subsequent adsorption of Me and $MeCpPtMe_2$ on identical oxidized monovacancies is endothermic but is made exothermic by pyridinic N dopants. Thus, the adsorption and dissociation of $MeCpPtMe_3$ is expected to occur more readily on N-doped substrates than undoped ones. We also experimentally demonstrated that elevated N and O content in mesoporous carbon supports causes $MeCpPtMe_3$ to deposit more platinum but only at increased temperature (300 °C).

AP-TuP-2 Subtractive Printing of Atomic Layer Deposition using Electrohydrodynamic Jet Printing*, **Tae Cho**, N. Farjam, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Traditional lithography requires multiple processing steps in a resource-intensive cleanroom environment. To overcome the limitations of traditional lithographic patterning and alignment, there has been tremendous interest in developing new methods for additive manufacturing. E-jet printing is an additive manufacturing technique which allows for fast and versatile printing with high resolution. Previously, e-jet printing was used to directly deposit functional materials on the surface with solution inks. Compared to this, ALD can deposit high-quality materials with unparalleled control of film thickness and uniformity at relatively low temperatures.

Our previous work has shown that by directly printing inhibitor polymers on the surface, we can locally activate/passivate atomic layer deposition (ALD) growth for area-selective ALD (AS-ALD) [1,2]. This technique allows customizable patterns with different geometries and high resolution without the need for premade alignment masks. However, AS-ALD may suffer from defect growth and/or vapor-phase-infiltration through the inhibitor polymers which can cause undesired growth on the surface. In this study, we demonstrate the use of subtractive electrohydrodynamic jet (e-jet) printing with acid-based ink to directly pattern the metal oxides deposited with ALD.

To pattern 50 nm thick ALD ZnO that was deposited on the silicon substrate, 0.1M hydrochloric acid mixed with glycerol was used as the ink for e-jet printing. When the ink was printed, glycerol residue was left behind on the surface after ink evaporation. After soaking the sample in water, the glycerol residue was washed away with ZnO; ZnO was removed on the printed regions, exposing the underlying silicon surface. Atomic force microscopy, scanning electron microscopy, and energy dispersive spectroscopy were performed to analyze the surface topology/chemistry after patterning the ZnO layer. With e-jet, linewidth and etched depth can be precisely controlled with printing speed and the number of printed layers. This new technique can provide flexible and customizable patterning of metal oxides without the need for AS-ALD or lithography.

[1] T.H. Cho, N. Farjam, C. R. Allemang, C. P. Pannier, E. Kazyak, C. Huber, M. Rose, O. Trejo, R. L. Peterson, K. Barton, N. P. Dasgupta, *ACS Nano* **14**, 17262 (2020)

[2] N. Farjam, T.H. Cho, N. P. Dasgupta, K. Barton, *Appl. Phys. Lett.***117**, 133702 (2020)

[3] T. H. Cho, N. Farjam, K. Barton, N. P. Dasgupta, *In preparation* (2022)

AP-TuP-4 Design of Gas Flow Field for a Sustainable ALD Process Chamber*, **Kyung-Hoon Yoo**,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; G. Song,* KUMYOUNG ENG Inc., Republic of Korea*; C. Kim,* TNG Co., Republic of Korea*; J. Hwang, H. Lee,* Korea Institute of Industrial Technology, Republic of Korea*; K. Lee,* SAMSUNG DISPLAY, Republic of Korea

In order to develop a sustainable ALD process cluster tool, it is necessary to establish a manufacturing technology for a high-productivity high-efficiency ALD process chamber that reduces the intrinsic excessive consumption of energy and materials.[1] In the present study, as the part of countermeasure to the excessive consumption, a micro-gap ALD process chamber is considered for the optimized design. The changes in the flow field of nitrogen in the process space of the process chamber with the gap sizes of 1 mm and 10 mm respectively are observed at 200 °C, utilizing computational fluid CFD numerical analysis. For the present nitrogen flow field with a background pressure of 1 Torr and a temperature of 200 °C, the Knudsen number Kn<0.1 and Reynolds number Re<<2300 are evaluated, and consequently the continuity and momentum equations of a steady-state compressible laminar flow field are considered.[2]

Acknowledgment

This work was supported by the Korean Ministry of SMEs and Startups, under Award no. S2960951.

References

[1] C.Y. Yuan and D.A. Dornfeld, 2010, *J. of Manufacturing Science and Engineering*, 132, 030918 (2010).

[2] M. R. Shaeri, T.-C. Jen, C. Y. Yuan and M. Behnia, *International Journal of Heat and Mass Transfer*, 89, 468 (2015).

AP-TuP-5 Atomic Structure Characterization of PEALE Semiconductors by Using HRSTEM*, **Chien-Nan Hsiao**, C. Chen,* National Applied Research Laboratories, Taiwan*; W. Chen,* National applied research Laboratories, Taiwan*; F. Chen,* National Applied Research Laboratories, Taiwan

An in-situ plasma enhanced atomic layer etching system has been design and fabricated. N_2O , BCl_3 and Ar plasma were used as the precursor for advanced semiconductor at various temperature. The optical detector was used to in-situ monitor the plasma spectrum during the step by step etching process. The AlGaN/GaN hetrostructure and MoS2 2D materials etching per cycle of ALE were investigated using an aberration-corrected scanning transmission electron microscope with energy distribution spectrometer. It is found that the layer by layer etching feature shows the process is a controlled self-limited reaction. The saturation curve of atomic etching rate and precursor pulsed time has been established. The etching per cycle of AlGaN is around 0.33 nm.In addition, the influence of various aberration coefficients such as defocus, astigmatism, coma, spherical aberration and star aberration on the shape of the probe and more importantly on the electron intensity distribution within the probe was calculated. The accuracy required for compensation of the various aberration coefficients to achieve sub-angstrom resolution (0.078 nm) with the electron optics system was evaluated by the calculation of phase shift. The (100) lattice spacing of MoS2 2D materials is around 0.274nm.

Nanoscale Science and Technology Division
Room 304 - Session NS+AP+BI+SS-WeM

Frontiers in Scanning Probe Microscopy Including Machine Learning

Moderators: Wonhee Ko, University of Tennessee, Knoxville, **Adina Lucian-Mayer**, University of Ottawa, Canada

8:40am **NS+AP+BI+SS-WeM-3 Decay Rate Spectroscopy for a Direct Probe of Josephson and Andreev Currents on the Atomic Scale*, Wonhee Ko,*** University of Tennessee, Knoxville*; J. Lado,* Aalto University, Finland*; E. Dumitrescu, P. Maksymovych,* Oak Ridge National Laboratory

The tunneling current in superconducting tunnel junctions involves several mechanisms in addition to the normal-electron tunneling, such as Josephson tunneling and Andreev reflection. Identification of the tunneling mechanisms as a function of external parameters, such as barrier height, bias voltage, temperature, and so on, is the key to elucidating the characteristics of the superconductors, such as paring symmetry and topology. Here, we present a method to identify distinct tunneling modes based on the decay rate of tunneling current measured by scanning tunneling microscopy (STM) [1,2]. Precise control of the tip-sample distance in picometer resolution allows us to quantify the decay rate as a function of bias V and tip height z, with which we identified the crossover of tunneling modes between single-charge quasiparticle tunneling, (multiple) Andreev reflection, and Josephson tunneling. The method was both applied to S-I-S [1] and S-I-N [2] junctions, to unambiguously identify Josephson and Andreev currents. Moreover, mapping decay rates in the atomic resolution with STM revealed the intrinsic modulation of Andreev reflection and Josephson current. The result shows that the decay rate spectroscopy will be crucial for addressing the superconducting characteristics of the materials and their applicability for Josephson-junction devices.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

[1] W. Ko, E. Dumitrescu, and P. Maksymovych, *Phys. Rev. Res.***3** 033248 (2021)

[2] W. Ko, J. L. Lado, and P. Maksymovych, *Nano Lett.***22** 4042 (2022)

9:00am **NS+AP+BI+SS-WeM-4 Machine Learning-Driven Automated Scanning Probe Microscopy: Application to Ferroelectric Materials*, Yongtao Liu,*** *K. Kelley, R. Vasudevan,* Oak Ridge National Laboratory, USA*; H. Funakubo,* Tokyo Institute of Technology, Japan*; S. Kalinin,* University of Tennessee Knoxville*; M. Ziatdinov,* Oak Ridge National Laboratory, USA

Scanning probe microscopy (SPM) has become a mainstay of many scientific fields including materials science, condensed matter physics, and so on. Machine learning (ML) and artificial intelligence (AI) have been applied to determine the physical mechanisms involved in phenomena encoded within microscopy data, enabling ML/AI to rapidly become an indispensable part of physics research. However, the real-time connection between ML and microscopy—which enables automated and autonomous experiments for microscopy imaging and spectroscopy measurements—still lags. Until now, the search for interesting functionalities in microscopy experiments has been guided by auxiliary information from microscopy to identify potential objects of interest based on human intuition; the exploration and verification of physical mechanisms depend on human-based decision making, i.e., operators determine the parameters for subsequent experiments according to the previous experiment. Here, we developed ML-driven automated experiment (AE) scanning probe microscopy (SPM) workflow to learn the functionality and mechanism in materials in an automatic manner. We demonstrate the application of deep kernel learning and hypothesis learning based workflows by investigating ferroelectric materials, including studies of domain wall dynamics, domain switching mechanism, the conductivity of topological defects, and relationship between domain structure and local properties. Using these approaches, we observe larger hysteresis opening near 180^o domain walls due to the larger polarization mobility in the vicinity of the 180^o walls in a $PbTiO_3$ sample and find that the domain switching in a $BaTiO_3$ thin film is determined by the kinetics of the domain wall motion, etc. We implemented these approaches in SPM for ferroelectric materials investigation, however, the workflows are universal and can apply to a broad range of imaging and spectroscopy methods, e.g., electron microscopy, optical microscopy, and chemical imaging.

Acknowledgements: This work (implementation, measurement, and data analysis) was primarily supported by the center for 3D Ferroelectric Microelectronics (3DFeM), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences under Award Number DE-SC0021118. This work (ML development) was supported by the Center for Nanophase Materials Sciences, a US Department of Energy Office of Science User Facility.

9:20am **NS+AP+BI+SS-WeM-5 AVS Dorothy M. and Earl S. Hoffman Scholarship Talk: Direct Imaging of Light-Matter Interaction of 0-dimensional Excitonic Emitters using Tip-enhanced Scanning Probe Technique*, Kiyoung Jo*[1]**, *E. Marino, J. Lynch, Z. Jiang, N. Gogotsi,* University of Pennsylvania*; P. Schuck,* Columbia University*; N. Borys,* Montana State University*; C. Murray, D. Jariwala,* University of Pennsylvania

Strong light-matter interactions of 0-dimensional emitters on plasmonic Au substrate were explored using both contact and tapping mode tip-enhanced scanning probe micro-spectroscopy. The plasmonic tip engaged with contact mode couples with the excitonic dipole in CdSe-CdS nanoplatelets, leading to strong exciton-plasmon coupling. Unlike the contact mode, the directional propagation of surface plasmon polariton from the excitonic emission of the nanoplatelets on Au as wave-like fringe patterns was probed by taking advantage of the tapping mode. Since tapping mode operates a few nanometers away from the surface, the near-field photoluminescence with in-plane wavevectors can be collected, leading to form fringe patterns propagating from the quantum plate. Extensive optical simulations proved that the fringes are the result of standing wave formed between the tip and the nanoplatelets. The effect of excitonic dipole orientation and dielectric layers on the fringe patterns were investigated by the simulation which matched with experimental results. The fringe patterns were also observed in WSe2 nano-bubbles, and the CdSe/CdS nanoplatelet in SiO2/Si substrate which means the phenomenon is universal in 0-dimensional emitters and various substrates. We envision that the discovery excels in understanding in-plane near-field light signal transduction from 0-dimensional emitters toward nano and quantum photonics.

9:40am **NS+AP+BI+SS-WeM-6 Nanoscale Subsurface Depth Sensitivity of Contact Resonance Atomic Force Microscopy on Layered Films*, Gheorghe Stan,*** National Institute for Science and Technology (NIST)*; C. Ciobanu,* Colorado School of Mines*; S. King,* Intel Corporation

Probing the mechanical properties is one of the basic inquiries that can reveal the structure and integrity of an isolated material or multicomponent system. At the nanoscale, due to size constrains and defects, mechanical tests become even more relevant as the properties of a part may differ by those of the whole. Over years, contact resonance AFM (CR-AFM) has proved to be a reliable AFM-based technique for nanoscale mechanical property measurements. Mostly operated into the elastic modulus range from few GPa to hundreds of GPa, CR-AFM was used to test different materials and structures at the nanoscale and considered for discerning the mechanical response of subsurface inhomogeneities and buried domains. It remains, however, to directly prove the extent of its quantitative capabilities both in terms of elastic modulus and depth sensitivity. In this work, we develop a quantitative methodology to test the elastic modulus and depth sensitivity of CR-AFM against a set of low-k dielectric bilayer films with the top layer of various thicknesses. We have analyzed the measured contact stiffness as a function of load and film thickness with both a semi-analytical model and three-dimensional finite element analysis. Both analyses confirmed the expected elastic moduli of the layered structures and provided a robust quantitative estimation of the subsurface depth and material sensitivities of CR-AFM. We also developed a correlative measurement-model analysis to assess the convoluted contributions of the structural morphology and mechanical properties to the contact stiffness used by AFM-based subsurface imaging. The results explain the inherent difficulties associated with solving concurrently the material contrast and location of subsurface heterogeneities in nanomechanical subsurface imaging.

11:00am **NS+AP+BI+SS-WeM-10 The Impact of Temperature on Viscoelastic Properties of Nanoscale Domains Within Polymer Composites*, Bede Pittenger,*** *S. Osechinskiy, J. Thornton, S. Loire, T. Mueller,* Bruker Nano Surfaces

The behavior of polymer composites is controlled by the properties of the components as well as the microstructure of the material. Because confinement effects and interphase formation can alter properties of the

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[1] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

microphases, only measurements performed directly on the composite can provide the needed local property distribution. Mechanical properties of polymers are generally temperature (and time) dependent, so a full understanding requires measurements over a range of temperatures and frequencies. Ideally, one would like to observe the mechanical behavior of these microscopic domains while they pass through their glass transitions to appreciate the influence of size effects and confinement on time dependent mechanical properties.

Recently, Atomic Force Microscopy based nano-Dynamic Mechanical Analysis (AFM-nDMA) was introduced. Like bulk DMA, this mode provides spectra of storage and loss modulus across frequency and temperature, allowing construction of master curves through Time Temperature Superposition (TTS). In addition, it allows high resolution measurements localized to the microscopic structures within heterogeneous samples. This presentation will examine the capabilities of this new mode with examples in a wide range of polymers and composites.

11:20am **NS+AP+BI+SS-WeM-11 AFM Force Spectroscopy Combined with Machine-Learning Methods for Identifying Malaria Derived- EV Subpopulations***, **Irit Rosenhek-Goldian**, P. Abou Karam,* Weizmann Institute of Science, Israel*; T. Ziv,* Technion - Israel Institute of Technology, Israel*; H. Ben Ami Pilo, I. Azuri, A. Rivkin, E. Kiper, R. Rotkopf, S. Cohen,* Weizmann Institute of Science, Israel*; A. Torrecilhas,* Federal University of São Paulo, Brazil*; O. Avinoam,* Weizmann Institute of Science, Israel*; A. Rojas,* University of Costa Rica*; M. Morandi, N. Regev-Rudzki,* Weizmann Institute of Science, Israel

The Malaria (*Plasmodium falciparum*) parasite releases extracellular vesicles (EVs) which modulate the mechanical properties of the host red blood celland thus facilitate parasite action. It is understood that EVs are composed of sub-populations with different functions, but little is known of their nature and specialized function. Here, we report the use of Atomic Force Microscopy (AFM) imaging and puncture analysis, combined with state-of-the-art size separation techniques and several biochemical, microscopic and spectroscopic characterization techniques in an attempt to differentiate and characterize the different populations. Specifically, we subjected malaria-derived EVs to size-separation analysis, using Asymmetric Flow Field-Flow Fractionation (AF4). The fractions obtained were characterized by Cryo-transmission electron microscopy (cryo-TEM), and AFM which revealed the presence of two distinct EV subpopulations - small (10-70 nm) and large (30-500 nm). Proteomic analysis revealed that the small EVs were enriched in complement-system proteins and the large EVs with proteasome subunits. In addition, Förster resonance energy transfer (FRET)-based fusion assay showed that small EVs fused to early-endosome liposomes at significantly greater levels than large EVs. Finally, AFM puncture analysis characterized by unsupervised machine-learning verified the presence of two distinct fractions with respect to mechanical behavior which correlate with the EV size groupings. These results shed light on the sophisticated mechanism by which malaria parasites utilize EV subpopulations as a communication tool to target different cellular destinations or host systems.

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

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

[2] **AVS Graduate Research Awardee**

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 $D = 6.3 \pm 0.5 \cdot 10^{-20}$ cm^2/s and for oxygen in the plasma polymer at room temperature $D = 3.0 \pm 0.2 \cdot 10^{-23}$ 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 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.

Thin Films Division
Room 316 - Session TF2+AP+SE+SS-WeM
ALD and CVD: Surface Reactions, Mechanisms and Kinetics

Moderator: Jessica Kachian, Intel Corporation

8:00am **TF2+AP+SE+SS-WeM-1 Nucleation Enhancement of Ruthenium Atomic Layer Deposition Using Organometallic Molecules***, **Amnon Rothman**, D. Tsousis, S. Bent,* Stanford University

Atomic layer deposition (ALD) is an attractive surface-sensitive thin-film deposition technique used in advanced technologies such as microelectronics, catalysis, and energy applications. The self-limiting surface reactions during the ALD process promote the layer-by-layer growth mechanism, thus providing significant control over the film thickness and conformality. However, due to an island growth mechanism and nanoparticle formation, metal ALD on oxide surfaces can lead to poor-qualify films and display long nucleation delays. One of the main reasons for the nucleation delays can be attributed to the differences in the surface energy between metals and oxide surfaces. In this work, we study the nucleation enhancement of ALD ruthenium layers on Si substrates by using a single monolayer of trimethylaluminum (TMA) or diethylzinc (DEZ) preadsorbed on the substrate prior to deposition. The nucleation enhancement is demonstrated for ruthenium ALD using two different ALD precursors, cyclopentadienylethyl(dicarbonyl)ruthenium(II) (RuCpEt(CO)2) and bis(cyclopentadienyl)ruthenium(II) (RuCp2), with O2 as a counter reactant. The ruthenium ALD nucleation and growth mechanism were studied using scanning electron microscopy (SEM), ellipsometry and X-ray photoelectron spectroscopy (XPS), both on the treated and untreated substrates. The results show that pretreatments using organometallic molecules reduce the nucleation delay of the ruthenium layer. The surface pretreatment strongly influences the ruthenium nucleation, yielding up to a 1.5-fold and a 2.1-fold increase in the surface coverage of the metal while using RuCpEt(CO)2 and RuCp2, respectively. Interestingly, pulsing TMA or DEZ, with or without exposure to H2O, is equally effective. We hypothesize that the high coverage in the pretreated samples is attributed to an increase in the substrate's surface energy, enhancing the surface diffusion of nanoparticles and adatoms during growth. We confirm that exposure of organometallic molecules during ruthenium ALD using the precursors above introduces a potential pathway toward achieving high-quality ruthenium thin films.

8:20am **TF2+AP+SE+SS-WeM-2 Ald of Chalcogenide and III-V Materials for Memory Applications***, **Laura Nyns**, A. Delabie, W. Devulder,* IMEC, Belgium*; J. Girard,* Air Liquide, France*; B. McKeown, V. Pallem,* Air Liquide*; T. Peissker, J. Sinha,* IMEC, Belgium*; N. Stafford,* Air Liquide*; J. Swerts,* IMEC, Belgium **INVITED**

To enable fast and powerful storage solutions for next generation mobile applications and other innovative technologies, the memory landscape focuses on various concepts. These concepts include DRAM for high-speed access, NAND flash memory for storage of large amounts of data, and the emerging Storage Class Memories (SCM) for massive data access in short time. Each of these technologies require their own set of materials with specific characteristics. Additionally, material deposition can be challenging because of the high aspect ratios which are typical for these advanced 3D architectures. Atomic Layer Deposition (ALD) has been shown to be a promising technique in that respect, as conformal deposition of a wide range of materials in complex topographies was established over the past decades. In this talk, we will address the ALD of germanium chalcogenides, a class of materials which is being explored as phase change memory and selector elements for SCM applications. GaAs will also be discussed, due to the need for high mobility channel materials to replace poly-Si in NAND flash technologies. We used the dechlorosilylation chemistry for the ALD of chalcogenide and III-V materials, where (nonmetal) alkylsilyl compounds react with metal chlorides to enable the growth of amorphous layers at low deposition temperatures [1]. An ALD GaAs process could be established, resulting in smooth and stoichiometric films that are amorphous as deposited. Crystallization into the preferred cubic phase was obtained at 350-400˚C, despite the presence of a Ga-rich surface oxide due to air exposure. Irrespective of the excellent step coverage in high aspect ratio structures, we found that these films are prone to delamination. We encountered a comparable challenge with ALD GeSe and $Ge_2Sb_2Te_5$ (GST) using this chemistry, and could demonstrate the benefit of proper surface treatments prior to film deposition to engineer the interface structure and improve layer adhesion. For GeSe, the extension of the existing ALD process [2] to ternary and even quaternary compounds is needed to boost the memory cell performance. We will therefore report on the development of an ALD process targeting GeAsSe deposition. Finally, we explored area-selective deposition (ASD) of chalcogenide materials, as this could greatly simplify the fabrication of complex 3D SCM devices. Our results indicate an impressive selectivity of 96% for GST films of ~22nm on TiN compared to SiO_2, by using the dechlorosilylation chemistry in combination with a dimethylamino-trimethylsilane (DMA-TMS) surface treatment.

[1] Pore et al, ***J. Am. Chem. Soc.***, 2009, **131**, 3478-3480

[2] Haider et al, ***Mater. Adv.***, 2021,**2**, 1635-1643

9:00am **TF2+AP+SE+SS-WeM-4 Plasma-enhanced Spatial ALD of SiO_2 investigated by gas-phase Infrared and Optical Emission Spectroscopy***, M. Mione, V. Vandalon,* Eindhoven University of Technology, Netherlands*; A. Mameli,* TNO-Holst Centre & Eindhoven University of Technology, The Netherlands*; F. Roozeboom,* TNO-Holst Centre & Eindhoven University of Technology, Netherlands*;* ***Erwin Kessels,*** Eindhoven University of Technology, Netherlands

A spatial atomic layer deposition (ALD) process for SiO_2 using bisdiethylaminosilane (BDEAS, $SiH_2[N(C_2H_5)_2]_2$) and an atmospheric O_2 plasma is reported as well as an investigation of its underlying reaction mechanisms [1]. Within the substrate temperature range of 100-250 °C, the process demonstrates self-limiting growth with a growth-per-cycle between 0.12 and 0.14 nm and SiO_{-2} films exhibiting material properties *on par* with those reported for low-pressure plasma-enhanced ALD (PEALD) [2].

Gas-phase infrared spectroscopy on the reactant exhaust gases and optical emission spectroscopy on the plasma region are used to identify the species that are generated in the ALD process. Based on the identified species and a calibration procedure, we propose a reaction mechanism where BDEAS molecules adsorb on –OH surface sites through the exchange of one of the amine-ligands upon desorption of diethylamine (DEA, $HN(C_2H_5)_2$). The remaining amine ligand is removed through combustion reactions activated by the O_2 plasma species leading to the release of H_2O, CO_2, CO in addition to products such as N_2O, NO_2, and CH-containing species. These volatile species can undergo further gas-phase reactions in the plasma as indicated by the observation of OH*, CN* and NH* excited fragments in emission. Furthermore, the infrared analysis of the precursor exhaust gas indicated the release of CO_2 during precursor adsorption. Moreover, this analysis has allowed the quantification of the precursor depletion yielding values between 10 % and 50 % depending on the processing parameters. On the basis of these results, the overall surface chemistry of the spatial ALD process of SiO_2 will be discussed.

[1] M. Mione, V. Vandalon, A. Mameli, W.M.M. Kessels, and F. Roozeboom, J. Phys. Chem. C 125, 24945 (2021)

[2] G. Dingemans, C.A.A. van Helvoirt, D. Pierreux, W. Keuning, W.M.M. Kessels, J. Electrochem. Soc. 159, H277 (2012)

9:20am **TF2+AP+SE+SS-WeM-5 Role of Al in Enhancing Growth Rate and Crystallinity in Chemical Vapor Deposition of $Hf_{1-x}Al_xB_2$ Coatings Below 300 °C***,* ***Kinsey Canova***[1]*, S. Shrivastav, C. Caroff, L. Souqui, G. Girolami, J. Krogstad, J. Abelson,* University of Illinois at Urbana-Champaign

Transition metal diborides are desirable as hard, low-friction, and wear-resistant coatings for applications in extreme environments. To survive high temperatures, the coatings must have a very low rate of microstructural evolution and must resist oxidation, in particular the loss of boron via evaporation of boron oxide. We previously showed that amorphous HfB_2 films can be deposited by chemical vapor deposition (CVD) using a borohydride precursor, $Hf(BH_4)_4$. However, at T > 600 °C, those coatings crystallize and densify, which leads to cracking, and they oxidize readily. Here, we co-flow an aluminum precursor, trimethylamine alane (TMAA), to deposit ternary $Hf_{1-x}Al_xB_2$ alloy films by CVD at temperatures ≤ 300 °C. This affords excellent film deposition and properties: (i) Al incorporation substantially increases the reaction rate of the HfB_2 precursor, yet the growth still gives good conformal coverage over all surfaces in deep features. (ii) The as-deposited films are nanocrystalline, and the lattice parameters are consistent with a random alloy on the metal sublattice, as opposed to a mixture of HfB_2 and AlB_2 grains. (iii) No elemental Al is detected, so there is not a mechanically soft, low-melting phase. (iv) Annealing films to 700 °C in air creates an Al_2O_3 surface layer that protects the underlying film, and negligible grain growth is observed. To determine a cause of the enhanced growth rate, we performed a matrix of growth experiments vs. precursor pressures and temperature; the Al incorporation rate, which is proportional to TMAA flux, has the strongest effect on rates. We hypothesize that Al consumes the excess boron from the HfB_2 precursor – which contains four boron atoms for every Hf atom – and forms AlB_2. This overcomes the probable rate limiting step of HfB_2 deposition, i.e., the associative desorption of excess boron from the growth surface as $B_2H_{6,}$ and it is consistent with the improved film crystallinity. Finally, this study provides a guide to the parameters controlling growth rate and composition.

9:40am **TF2+AP+SE+SS-WeM-6 Pushing the Limits of ALD Infilling to Produce Macroscopic Nanocomposites***,* ***Benjamin Greenberg****, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) infilling is a reliable and popular technique for producing nanocomposite thin films. Typically, ALD precursor dose times on the order of 1 s are sufficient for infiltrating and conformally coating the pores of nanoparticle (NP) networks with thickness on the order of 1 µm or less. In principle, the application space for this nanocomposite production method could be expanded significantly by increasing the NP network thickness to 1 mm or greater. In this work, we investigate the possibility of achieving this scale-up through increasing the ALD precursor dose time by three orders of magnitude. We hydraulically press aluminum oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with ~2 mm thickness and ~50% solid volume fraction, and we coat the pores with either Al_2O_3 or ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for >1,000 s per half-cycle. For both coatings, we analyze the ALD chamber pressure traces to understand precursor diffusion and reaction kinetics, and we compare our results to predictions based on a Knudsen diffusion model. For the ZnO coating, we use electrical conductivity measurements, X-ray crystallography, scanning electron microscopy, and energy-dispersive X-ray spectroscopy to evaluate coating composition and uniformity within the nanocomposite, and we compare the ZnO-infilled-Al_2O_3 nanocomposite to a compact of core/shell Al_2O_3/ZnO NPs produced by particle ALD (pALD) in a rotary reactor. Preliminary data suggest that uniform infilling of a macroscopic NP network is possible provided that it can be carried out at a temperature sufficiently low to prevent precursor decomposition.

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

Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic
Room 301 - Session HI+AP-WeA
Emerging Ion Sources, Optics, & Applications

Moderators: Rosa Cordoba, University of Valencia, Spain, **Florian Vollnhals**, INAM, Germany

2:20pm **HI+AP-WeA-1 Rationalizing and Controlling the Composition and Properties of Materials Deposited Using Charged Particles*, Howard Fairbrother,*** Johns Hopkins University **INVITED**

Focused ion beam-induced deposition (FIBID) and focused electron beam-induced deposition (FEBID) are charged particle nanofabrication techniques able to directly fabricate 2D and 3D metal-containing nanostructures from organometallic precursors. These techniques provide for precise control over beam position for nanoscale pattern writing without the use of a mask or organic solvents and as such are more environmentally benign and less wasteful than traditional lithography techniques. However, one of the biggest issues with charged particle deposition techniques is the difficulty in controlling the composition of the deposits. Indeed, the creation of pure metal nanostructures in FEBID or FIBID is often a goal for achieving optimal materials properties, but is rarely realized in practice without the need for post deposition processing. In this presentation, and using Pt as an example, I will describe how UHV surface science studies can be used to aid in the design of precursors and selection of deposition conditions that favor the creation of pure metal deposits. Examples will include, (i) the electron beam induced deposition of Pt nanostructures from $Pt(CO)_2Cl_2$, where surface science studies have identified the two sequential steps which can lead to Pt formation, notably the initial deposition event ($Pt(CO)_2Cl_{2(ads)} + e^-$à $PtCl_{2(ads)} + 2CO_{(g)}$) as well as the subsequent removal of Cl via an ESD type process ($PtCl_{2(ads)} + e^-$à $Pt_{(ads)} + Cl^-_{(g)}$) and (ii) ion-beam induced deposition of Pt from $MeCpPtMe_3$ and $Pt(CO)_2X_2$ precursors, where surface science studies have revealed the greater utility of effecting deposition with lighter ions (e.g. H_2^+, He^+), due to their ability to access deposition conditions over which nearly pure Pt can be deposited as compared to heavier ions (e.g. Ar^+) where Pt sputtering rates preclude the formation of Pt. The microstructure and properties of these Pt deposits as well as the possibilities to use analogous approaches for the charged particle deposition of other metals (e.g. Au) will also be discussed.

3:00pm **HI+AP-WeA-3 Ion Beam Induced Reactions and Deposition of $Pt(CO)_2Br_2$ and $Pt(CO)_2Cl_2$*, Mohammed Abdel-Rahman,*** *P. Eckhert,* Johns Hopkins University*; J. Yu, A. Chaudhary, L. McElwee-White,* University of Florida*; H. Fairbrother,* Johns Hopkins University

Direct-write lithography techniques, such as focused ion beam induced deposition (FIBID), are an attractive alternative to traditional lithographic techniques. However, traditional precursors ($Me_3PtCpMe$, $Pt(acac)_2$, for chemical vapor deposition perform poorly as FIBID precursors and result in carbon-contaminated metal deposits. To overcome this limitation, $Pt(CO)_2X_2$ (X = Br, Cl) were chosen as alternative precursors because of its low carbon content and desirable volatility for FIBID. FIBID deposits were created from commercially available $Pt(CO)_2Cl_2$ and lab synthesized $Pt(CO)_2Br_2$, complemented by *in situ* UHV studiesusing XPS and MS to determine the sequence of ion-induced processes that underly the deposition mechanism. Deposition and UHV studies were conducted with Ar^+, He^+, and H_2^+ to determine the effect of ion properties (mass and reactivity) on the deposition process. Results obtained on thin films of precursors molecules deposited on inert substrates at temperatures < 200K under UHV conditions indicate that, regardless of the ion or precursor, the deposition mechanism proceeded via rapid and complete CO loss forming PtX_2. Subsequent reactions are dominated by sputtering of the PtX_2 species with halogen loss proceeding quicker than Pt loss. Consequently, pure Pt deposits are formed beyond a critical ion dose. Although varying the ion does not alter the deposition mechanism, the relative reaction rates for the deposition and sputtering processes increase with ion size following the pattern $Ar^+ > He^+ > H_2^+$. This information can be used to select the steady-state conditions best suited to form pure Pt deposits in the absence of post-deposition purification steps.

3:20pm **HI+AP-WeA-4 Next Generation Ion Beam Resists: Sub-10 nm Helium Ion Beam Lithography*, Scott Lewis,*** *G. Derose,* California Institute of Technology

A new class of metal organic resist materials that is based on a heterometallic ring (Figure 1) has been demonstrated with helium ion beam lithography while demonstrating extraordinarily high etch selectivity for silicon of >5:1 (at 8 nm half pitch (HP)) when subjected to a pseudo-Bosch inductively coupled plasma–reactive-ion etch (ICP-RIE). The resist was designed using our latest Monte Carlo simulator (Figure 2a), which we developed because there are no simulators for ion beam lithography. Ion simulation packages such as SRIM/TRIM provide accurate data for ion penetration and propagation into a material for applications such as ion implantation, it fails to provide data on the creating a secondary electron (SE) and creating SE’s cascade with further orders of SE’s which are essential as they will have large effect on the sensitivity of the resist and will have a large contribution on the proximity effect. Exposing the resist to 35 keV helium ions, produced a nano pattern with a resolution of 8.5 nm HP (Figure 2b and c for a plan and tilted view), and obtained a low exposure dose of 22 pC/cm. This dose is 3 orders of magnitude lower than what is required with EBL when comparing to 100 and 30 keV electrons. To account for the low doses, this talk describes how the helium ion interacts with the resist and shows that the exposure mechanism occurs in two parts. Firstly, the helium ions are confined to the incident beam because of the resist properties of high molecular weight and low density limits the number of scattering sites that the ion encounters. Secondly, the helium ion interaction yields significantly more SE’s per incident ions than electrons which had a significant contribution to the exposure efficiency. This is why that a dose lower by three orders of magnitude when compared to electron beam lithography. Through Monte Carlo simulation and X-ray photoelectron spectroscopy we will explain how the resist achieves the extraordinary high dry etch selectivity seen here (Figure 2d) where the 8.5 nm HP pattern was successfully transferred via the dry etching process into the silicon substrate. We will show through the use of Monte Carlo simulations how we were able to dramatically improve the resist by increasing its sensitivity and improving its LER while maintaining the same resolution and its high dry etch electivity. The resist has demonstrated the flexibility to be exposed by ions, electrons and EUV, which makes it a versatile lithographic material with the potential for further customization to address a wide range of nanofabrication challenges.

4:20pm **HI+AP-WeA-7 Novel Source Development for Focused Ion Beam Implantation and Irradiation*, Edward S. Bielejec,*** *M. Titze, A. Katzenmeyer, A. Belianinov,* Sandia National Laboratories*; Y. Wang,* Los Alamos National Laboratory*; B. Doyle,* Sandia National Laboratories **INVITED**

We will present on Sandia National Laboratory’s Ion Beam Laboratory (IBL) development of novel sources for focused ion beam implantation and irradiation capabilities.The IBL operates seven focused ion beam (FIB) systems that range in ion energy from less than 1 keV to greater than 70 MeV, including a wide range of ion species from protons (H) to lead (Pb) over a range of spot sizes from nm to mm.In particular, we will concentrate on the development of liquid metal alloy ion sources (LMAIS) for our two mass filtered FIB systems, the A&D nanoImplanter and the Raith Velion, both of which include high spatial resolution with CAD based patterning to enable the formation of arbitrary patterned implantation.

We will present an overview of the available LMAIS for the mass filters systems as well asfabrication details and results using both novel Pb and N sources.The Pb source is based on a SnPb alloy using a custom Kovar wire tip in place of the standard tungsten tip usually used for FIB applications.This source has demonstrated a long lifetime comparable to our other alloy-based sources of greater than 2000 mA*hr and less than 50 nm resolution without optimization of the tip design.The atomic N source is based on an AuSn alloy implanted with nitrogen up to the saturation limit and verified using elastic recoil detection (ERD).This N source has demonstrated a relatively short lifetime of less than 100-200 mA*hr and is limited to a total N ion production rate of approximately 2,000 to 10,000 ions/s corresponding to up toapproximately 1 fA of current of singly charged nitrogen ions.The demonstration of these sources works to continue the development of high resolution localized implantation and irradiation capabilities enabling the fabrication of custom implanted samples for cutting edge physics and quantum optics experiments.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

5:00pm **HI+AP-WeA-9 Focused Ion Beams from GaBiLi LMAIS for Nanofabrication and Ion Imaging***, **Torsten Richter**, P. Mazarov, A. Nadzeyka, L. Bruchhaus, U. Mantz,* Raith GmbH, Germany

Focused Ion Beams (FIB) are broadly used in nanoscale science related applications, and they are inherently applied for direct nano-patterning, nanofabrication as well as for nano-analytics. FIB has become established as a direct, versatile, and precise fabrication method of smallest features at high fidelity. High demands are made on the ion beam that is used for direct FIB in terms of beam stability, patterning resolution and adjusting of the sputter yield. Liquid Metal Alloy Ion Source (LMAIS) is an emerging FIB source technology that provides a versatile solution to deliver various ion species from a single source for FIB nanofabrication to enhance resulting nanostructures [1]. However, beside nanofabrication FIB is utilized as a primary beam for SIMS analysis [2] and light ions such as Lithium in particular are well suited for sample imaging due to their low sputter yield and surface sensitive properties.

GaBiLi ion sources provide light and heavy ions from a single Liquid Metal Alloy Ion Source (LMAIS) fulfil requirements for both nanofabrication and nano-analytic [3]. Lithium, Gallium and Bismuth ions are emitted simultaneously, and ion species are separated subsequently in an ExB filter. Therefore rapid, easy, and reliable switching between light Lithium ions, and heavy Bismuth or Gallium ions enables not only novel nanofabrication processes but also satisfies analytical demands. GaBiLi allows 3D mill&image by imaging at highest lateral resolution by light Li ions and permits sample delayering at highest depth resolution with Bi ions or even Bi clusters [4]. SIMS takes advantage of optimizing either sputter yield or ionization yield of ejected ions.

In this contribution we present an overview of direct nanopatterning applications and related workflows such as 2-step bowtie nanofabrication with Lithium and Bismuth from GaBiLi (Figure 1) and ion beam imaging results that were obtained with Lithium ions (Figure 2).

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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. A. Mameli, ACS Appl. Mater. Interfaces, 2018, 10
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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**[12], 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-

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

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

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 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.

References

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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 $CuN_{0.3}$.

Thin Films Division
Room 316 - Session TF1+AP-WeA
Manufacturing and Scale-Up of CVD and (Spatial) ALD

Moderators: Joe Becker, Kurt J. Lesker Company, **Marceline Bonvalot**, Grenoble Alpes University, France

2:20pm **TF1+AP-WeA-1 Optimizing Vapor Delivery of a Nickel Diazadienyl Complex for Nickel Metal Atomic Layer Deposition***, J. Maslar, **Berc Kalanyan**,* NIST-Gaithersburg*; V. Dwivedi,* NASA*; D. Moser,* EMD Electronics

Nickel metal films find applications in numerous areas, including microelectronics and heterogeneous catalysis.In the case of microelectronics in particular, a nickel metal thermal deposition process that can produce high-purity, thin, conformal films at low deposition temperature is highly desirable.Atomic layer deposition (ALD) is widely used to deposit thin, conformal films when suitable precursors are available.However, because nickel is an electropositive metal, many of the combinations of reducing agent and metal precursor classes employed in more traditional metal thermal ALD processes are not suitable for Ni ALD.In contrast, transition-metal diazadienyl complexes represent a class of precursors that has been used successfully for metal thermal ALD, with the deposition of nickel films achieved using bis(1,4-di-*tert*-butyl-1,3-diazadienyl)nickel [$Ni(DAD)_2$].[1]A complicating factor in the reproducible deposition of nickel metal films with $Ni(DAD)_2$ is that this precursor is a solid at typical delivery temperatures and, in general, delivering a constant flux of a solid precursor can be difficult.Flux variations may not be an issue for an ideal ALD process unless the total precursor dose is insufficient to saturate all surface reactive sites, however, it is not clear what delivery conditions are necessary to provide consistently saturating $Ni(DAD)_2$ doses.The goal of this investigation is to optimize $Ni(DAD)_2$ delivery for nickel ALD and to identify any factors that may lead to irreproducible delivery.To achieve this goal, the dependence of the flux of both $Ni(DAD)_2$ and the DAD ligand (the primary decomposition product under the conditions of this study) on delivery conditions was characterized.The flux of each species was measured simultaneously using a two-channel gas analyzer which employed a broadband ultraviolet-visible source, a beam splitter, bandpass filters for wavelength isolation, and avalanche photodiode detectors.While the results of this investigation specifically apply to $Ni(DAD)_2$ delivery, it is expected that these results should also provide insight into optimizing delivery of other transition-metal diazadienyl complexes, as well as solid precursors in general.

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2:40pm **TF1+AP-WeA-2 Mechatronic Spatial Atomic Layer Deposition: Model-Informed Design for Scalable Manufacturing***, **Daniel Penley**, T. Cho, O. Trejo, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Spatial atomic layer deposition (SALD) holds promise to address the large-scale manufacturing needs of interfacial engineering at the nanoscale. However, the many SALD systems are limited in their ability to tune and dynamically control the full range of key process parameters, such as the depositor head and substrate gap size and parallel alignment. This lack of mechatronic control limits the ability to examine the coupled chemical, thermal, and transport phenomena as a function of SALD process parameters. Additionally, there have been several previous efforts to computationally model the SALD processes. However, there is a general lack of experimentally-validated models to verify the effects of systematically tuning the multitude of process parameters during SALD growth.

Herein we describe a customized SALD system that enables mechatronic control of key process parameters. A showerhead depositor design effectively delivers precursor to the substrate surface while stepper motors and capacitive probes maintain gap size and parallel alignment through multiple axis tilt and closed-loop feedback. Precision motorized stages control the substrate velocity and positioning, *in situ* monitoring actively controls the gas flow rates, and a thermal management system controls process temperature. We developed a three-dimensional COMSOL

Multiphysics model to understand the pressure, velocity, and concentration fields of the precursor gas flow within the system geometry. The capability to tune process parameters both physically and digitally allows for the unique ability to experimentally validate and parameterize the computational model to gain further insight into the otherwise difficult to access process area of close-proximity SALD. Using this linked experimental and modeling approach, we demonstrate the model's ability to predict resulting films from the mechatronic SALD system. With the experimentally-validated model and system, we present a study of the impact of SALD process parameters on the uniformity and quality of deposited SALD films. We then broaden our findings to discuss design implications SALD system design on the manufacturing tradeoffs of quality-throughput-cost-sustainability.

3:00pm **TF1+AP-WeA-3 Atmospheric Pressure Spatial ALD of Al-Doped ZnO: Co-injection vs. Supercycles***, **Mike van de Poll**, B. Macco, E. Kessels,* Eindhoven University of Technology, Netherlands

Atmospheric pressure spatial atomic layer deposition (ALD) is particularly interesting for high volume, low cost applications, because of its exceptionally short deposition times compared to temporal ALD.

For doped and compound materials, such as transparent conductive oxides, the electrical and optical properties are typically closely related to their composition. This makes accurate compositional control essential for high quality films. Spatial ALD of doped and compound materials generally follows one of two approaches. Supercycles can be formed by alternating two ALD cycles with different precursors, where the ratio between both cycles determines the composition of the deposited film. Alternatively, in the so called co-injection approach, the precursors can be dosed simultaneously. Here, the composition is determined by the precursor flows ratio.

In this work, ZnO:Al thin films were deposited using spatial ALD, with diethylzinc (DEZ) and dimethylaluminum isopropoxide (DMAI) as zinc and aluminum precursors, respectively, and H_2O as co-reactant. The supercycle and co-injection approaches were used, and the cycle ratio and mixing ratio were varied to alter doping concentrations. The films were capped with a layer of Al_2O_3 to shield from the ambient, and to mitigate hydrogen effusion. Electrical and optical properties of the samples as-deposited, and after stepwise anneal, were extensively studied.

Co-injection and supercycles resulted in the successful deposition of ZnO:Al films with optical and electrical properties (e.g., resistivity = 1.73 mΩcm, mobility = 9.6 cm^2/Vs, carrier concentration = $3.75 \cdot 10^{20}$ cm^{-3}) similar to temporal ALD ZnO:Al. Furthermore, the extensive study of these approaches led to identification of their advantages and disadvantages. Co-injection results in films with low resistivity as-deposited, due to homogeneous distribution of dopants. However, obtaining low Al doping levels can be practically challenging because low DMAI flow is required. Meanwhile, supercycles give precise compositional control by changing the cycle ratio, but result in dopant planes with low doping efficiency, and post-deposition anneal is required. After annealing the results are similar to co-injection.

Currently, our work focusses on the innovative approach of co-injection supercycles. Here, pure DEZ and co-injection DEZ/DMAI cycles are alternated, allowing additional compositional control by tuning both the DMAI flow during the doping cycle, and the cycle ratio. With co-injection supercycles we aim to combine the advantages of both dosing approaches. Initial films have been deposited and the full study will be presented at the conference.

3:20pm **TF1+AP-WeA-4 Manufacturing of ALD-enhanced Li-ion Batteries via Particle ALD Coatings And R2R ALD on Separators***, **Markus Groner**, A. Dameron, B. Hughes, D. Lewis, J. Keene, M. Martinez, J. Burger, M. Rodgers, J. Ragonesi,* Forge Nano*; J. Li,* Oak Ridge National Laboratory, China*; W. Steenman, K. Livingston,* Oak Ridge National Laboratory

ALD processing equipment for coating anode, cathode, and separator materials at scale has been developed to demonstrate ALD-enhanced Li-ion battery manufacturing. The promising performance enhancements seem previously in coin cells for ALD coated anode and cathode powders are now being validated in pouch cells. Thin ALD coatings can stabilize graphite and NCM materials, yielding improved capacity retention and rate performance, especially at higher voltages. Particle ALD coating tools are available for coating powders at the tons-per-day scale, both in semi-batch and continuous ALD versions. Additionally, ALD coatings on separators enhance electrolyte wetting and thermal stability, which should lead to improvements in the time & energy intensive filling/formation/aging steps as well as safety. A true roll-to-roll ALD tool for coating separators with alumina ALD films has been designed and built. Over the next year, this R2R tool will be integrated with a slitter and a pouch cell stacker. The performance improvements of the ALD-coated anode and cathodes, combined with the benefits of R2R ALD-coated separator, promise reductions in the cost/time/energy of battery manufacturing via ALD-enhanced Li-ion batteries.

Quantum Information Science Focus Topic
Room 302 - Session QS+AP+EM+MN+NS+SS-ThM

Systems and Devices for Quantum Computing

Moderators: Vivekananda Adiga, IBM, T.J. Watson Research Center, **Kathy-Anne Soderberg**, Air Force Research Laboratory

8:00am **QS+AP+EM+MN+NS+SS-ThM-1 Effects of Environmental Radioactivity on Superconducting Qubits***, L. Cardani,* ***Ambra Mariani,*** Istituto Nazionale di Fisica Nucleare, Italy **INVITED**

Environmental radioactivity was recently discovered as a potential limit for superconducting quantum bits.

We review recent works proving that ionizing radiation lowers the coherence of singe qubits and induces correlated errors in qubits arrays. We also present preliminary studies showing that operating qubits in a low-radioactivity environment improves their performance. These results fuelled the interest of several European and US groups in further investigating and mitigating radioactivity for next-generation quantum processors.

Using radioactivity measurements and simulations, we estimated the separate contribution of "far" radioactive sources (cosmic rays and laboratory radioactivity) and close materials contamination (chip holder, magnetic shield, …) on a typical chip, focussing on a qubit prototype developed within the SQMS center. We present such contributions and discuss the possibility of mitigating them in "standard" qubit laboratories or, eventually, in deep underground facilities.

8:40am **QS+AP+EM+MN+NS+SS-ThM-3 Dynamics of a Dispersively Coupled Transmon in the Presence of Noise from the Control Line***,* ***Antti Vaaranta,*** Bluefors Oy, Finland*; M. Cattaneo,* University of Helsinki, Italy*; R. Lake,* Bluefors Oy

In this talk we present theoretical results from a complete description of transmon qubit dynamics in the presence of noise introduced by an impedance-matched resistor (50 Ohm) that is embedded in the qubit control line, acting as a noise source [1]. We derive a model to calculate the qubit decoherence rate due to the noise emanating from this noise source [2]. The resistor is treated, using the Caldeira-Leggett model, as an infinite collection of harmonic LC-oscillators making it a bosonic bath [3]. To obtain the qubit time evolution affected by this remote bath, we start with the microscopic derivation of the Lindblad master equation using the dispersive Jaynes-Cummings Hamiltonian with added inductive coupling to the bath. To solve the resulting master equation, we transform it into a block diagonal form by exploiting its underlying symmetries following Ref. 4. The block diagonalization method reveals that the long time decoherence rate is given by the slowest decaying eigenmode of the Liouvillian superoperator. Moreover, when the readout resonator is in the equilibrium thermal state, the rate of exponential decoherence of the qubit is almost exactly exponential for all times with the predicted rate given by the slowest decaying eigenmode. We also study how the decoherence rate depends on the temperature of the noise source and explore the strong and weak dispersive coupling regimes. The model captures the often used dispersive strong limit approximation of the qubit decoherence rate being linearly proportional to the number of thermal photons in the readout resonator. However, in the dispersive weak limit we predict remarkably better decoherence rates. The model parameters are completely determined by the values of the circuit components, allowing for the exact study of the dynamics on the level of each individual circuit element.

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[2] A. Vaaranta, Study of environmental effects on a dispersive transmon qubit, MSc thesis, Univ. of Helsinki, (2022).

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[4] M. Cattaneo et al., Phys. Rev. A 101, 042108 (2020).

9:00am **QS+AP+EM+MN+NS+SS-ThM-4 Accurate Microwave Characterization for Superconducting Quantum Technology***,* ***Slawomir Simbierowicz,*** Bluefors Oy, Finland

Recent breakthroughs in quantum technology have highlighted a need for methods for accurate characterization of cryogenic microwave devices at millikelvin temperatures. In this two-part talk, I will highlight recent progress on microwave measurements at the quantum device reference plane including: (1) system noise characterization of amplifier chains, and (2) calibrated S-parameters of qubit drive line components.In the first part, I will discuss an impedance-matched variable temperature noise source which can be installed in a coaxial line of a cryostat. Using the method of hot/cold source with many input noise temperature points, the system noise temperatures of qubit readout amplifier cascades can be determined. I present measurement results in terms of added noise in Kelvins or photons from a four-wave (4WM) mixing traveling wave parametric amplifier (TWPA) [1], a Josephson parametric amplifier [2], 3WM TWPA, and high electron mobility transistor amplifiers [1].In the second part of the talk, I will present measurements of the 1-port S-parameters of qubit drive line components using a data-based short-open-load calibration at a temperature of 30 mK [3]. The measurement enables us to model systematic errors in qubit state preparation due to non-idealities in qubit control lines such as impedance mismatch. We model the results using a master equation simulation of all XY gates performed on a single qubit. Our work directly addresses the gap between electrical engineering parameters of individual measurement components and performance of the quantum device itself.

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[2] Mustafa Bal et al., "Overlap junctions for superconducting quantum electronics and amplifiers", Appl. Phys. Lett. **118**, 112601 (2021)

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9:20am **QS+AP+EM+MN+NS+SS-ThM-5 Improving Qubit Performance Through Engineering of the Substrate-Josephson Junction Interface***,* ***Cameron Kopas,*** *H. Cansizoglu, R. Cochrane, B. Ercan,* Rigetti Computing*; D. Goronzy, C. Torres-Castanedo,* Northwestern University*; J. Oh,* Ames Laboratory*; A. Murthy,* Fermi Lab*; E. Lachman,* Rigetti Computing*; A. Romanenko, A. Grassellino,* Fermi Lab*; M. Kramer, L. Zhou,* Ames Laboratory*; M. Bedzyk,* Northwestern University*; J. Mutus,* Rigetti Computing*; M. Hersam,* Northwestern University*; K. Yadavalli,* Rigetti Computing **INVITED**

The performance of a superconducting qubit is often limited by dissipation and two-level systems (TLS) losses. The dominant sources of these losses are believed to come from interfaces and surfaces, likely as a result of fabrication processes, materials, or atmospheric exposure. We show that certain chemical surface treatments can be used to modify the silicon surface before Josephson junction deposition, reducing the number of strongly-coupled TLS, and improving T1. While identifying specific microscopic sources for loss and TLS is still an open question, targeted characterization of test structures will show which physical changes correlate with performance improvements. We report chemical, structural, and low-temperature microwave characterization of superconducting qubits and films fabricated with different Si surface treatments.

11:00am **QS+AP+EM+MN+NS+SS-ThM-10 Design and Optimal Control of Superconducting Qubits to Achieve Quantum Speed Limits***,* ***Meenakshi Singh,*** Colorado School of Mines, USA **INVITED**

Fast two-qubit entangling gates are essential for quantum computers with finite coherence times. The finite interaction strength between qubits introduces a theoretical speed limit on the speed of these two-qubit entangling gates. This speed limit has been analytically found only for a two-qubit system under the assumption of negligible single qubit gate times. Here, we demonstrate such a speed limit experimentally using optimal control on two superconducting transmon qubits with a fixed capacitive coupling and finite single qubit gate times. Furthermore, we investigate the effect of additional couplings on the speed limit, both through introduction of an ancillary qubit as well as through utilization of higher transmon energy states. Finally, we discuss the generalization to many qubit systems where properly leveraging all available couplings can provide dramatic speedups.

11:40am **QS+AP+EM+MN+NS+SS-ThM-12 Atomic Scale Processing for Quantum Computing***, **Harm Knoops,*** Oxford Instruments Plasma Technology, Netherlands **INVITED**

With the increasing technological readiness of quantum technology (QT) the field has to start focussing on scalable fabrication methods for quantum bits (qubits) and quantum circuits. This contribution will focus on the enabling role atomic scale processing (ASP) methods such as atomic layer deposition (ALD) and atomic layer etching could play in scaling of QT. The main focus will relate to superconducting qubits and processing of superconducting nanolayers.

Superconducting nanolayers (metals, metal-nitrides) are required for various roles in QT including use in resonators, single-photon detectors, and interconnects.[1] The electrical contacts needed to control the qubits will require non-planar connectivity using superconducting interconnects.[2]Adequate routes for fabrication of planar superconducting layers exist, but for 3D interconnects or through-silicon vias (TSVs), the excellent conformality of ALD nanolayers could be essential. Although for resonators conformality is not a challenge, ALD's thickness control and uniformity should allow high-quality resonators with low spread in properties. For these superconducting nanolayers, metal-nitride compounds have been identified as particularly promising since they exhibit limited surface oxidation (compared to pure metals such as Nb), combined with relatively high critical temperature (T_c) for superconductivity (e.g., as compared to Al). Despite the challenges that the synthesis of high-quality nitrides pose, plasma ALD has demonstrated the capability to deposit high-quality nitrides (e.g., low O content, high electrical conductivity).[3] Furthermore, substrate-biased plasma-ALD offers unique opportunities to obtain and tune high-quality nitrides.[4] For removal of surface oxides or smoothing of resonator surfaces and interfaces, approaches combining ALD and ALE could be of interest.[5] Both ALD and ALE are envisaged to be key tools to allow scaling of these devices and advance the QT field.

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Thin Films Division
Room 316 - Session TF+AP-ThM
Novel ALD CVD Precursors, Processes, Deposited Morphologies and Substrate Architectures

Moderators: Parag Banerjee, University of Central Florida, **Richard Vanfleet**, Brigham Young University

11:00am **TF+AP-ThM-10 The Electrical and Magnetic Properties of Nonstoichiometric Nickel Oxide Thin Films***, **Mari Napari,*** University of Southampton, UK **INVITED**

Nonstoichiometric nickel oxide (NiO_x), a p-type oxide semiconductor, has gained significant attention due to its versatile and tunable properties. It has become one of the critical materials in wide range of electronics applications and highly sensitive and selective sensors. In addition, the wide band gap and high work function, coupled with the low electron affinity, have made NiO_x widely used in emerging optoelectronics and p-n heterojunctions [1,2]. Also, it is a commonly applied material in heterogenous catalysis. The properties of NiO_x thin films depend strongly on the deposition method and conditions. Efficient implementation of NiO_x in next-generation devices will require controllable growth and processing methods that can tailor the physical, electronic, and magnetic properties of the material.

In this presentation I discuss our work that links together the fundamental electronic properties of NiO_x thin films with the chemical processing methods, and how these can be used in device applications. I discuss how the p-type nature of NiO_x arises and how its stoichiometry affects its electronic properties, and present results that show how the antiferromagnetic nature of the NiO prevails also in the non-stoichiometric films. I will present examples of NiO_x thin films grown by the chemical deposition techniques, including CVD, ALD, and solution processing approaches, and show how these films can successfully be used in a range of devices and applications, including perovskite solar cells and photoelectrocatalysis [3,4].

[1] Napari et al. "Antiferromagnetism and p-type conductivity of nonstoichiometric nickel oxide thin films" InfoMat 2 (2020) 769-774

[2] Napari et al. "Nickel oxide thin films grown by chemical deposition techniques: Potential and challenges in next-generation rigid and flexible device applications" InfoMat 3 (2021) 536-576

[3] Zhao et al. "In Situ Atmospheric Deposition of Ultrasmooth Nickel Oxide for Efficient Perovskite Solar Cells" ACS Appl. Mater. Interfaces 10 (2018) 41849-41854

[4] Innocent et al. "Atomic scale surface modification of TiO_2 3D nano-arrays: plasma enhanced atomic layer deposition of NiO for photocatalysis" Mater. Adv. 2 (2021) 273-279

11:40am **TF+AP-ThM-12 Al_2O_3 Thin Films with Controlled Nanoporosity Prepared by Low Temperature Thermal ALD***, **Marceline Bonvalot**, S. Hekking,* LTM - MINATEC - CEA/LETI, France*; C. Vallée,* SUNY POLY, Albany

Because Al_2O_3 is a cheap and abundant material with a very high hardness and inertness to numerous chemicals, porous alumina thin films find a great variety of applications as a filtering material of liquids in the food industry, oil and gas industry, pharmaceutical industry and in biotechnologies as well. In this work, we describe an original experimental route, which leads to the production of Al_2O_3 thin films with controlled nanoporosity. The deposition is carried out by thermal ALD with trimethyl aluminum (TMA) as precursor and at low temperatures (between 50°C and 80°C). The process temperature is deliberately set below the precursor temperature window, so that a significant amount of carbon-rich contaminants remain in the produced thin film, due to poor decomposition of the precursor at low thermal energy. An intermediate O_2 plasma step is then inserted within the thermal ALD cycles, which helps for the degassing of these contaminants leaving behind nanoscale porosities within the thin film under growth. The process optimisation will be presented by discussing the impact of incident plasma power and duration on carbon-rich contamination levels. The frequency of the occurence of the O_2 plasma step inserted within the thermal ALD process will also be investigated, and discussed in regards to imperfectly perfect materials strategies.

12:00pm **TF+AP-ThM-13 Thermal ALD Process of NiO Based on Ni(^{t}Bu-MeAMD)$_2$ Precursor***, **Cristian van Helvoirt**, N. Phung, M. Creatore,* Eindhoven University of Technology, Netherlands

The applications of NiO thin films have increased over the last years, especially in the fields of electrocatalysis for water-splitting [1] and metal halide perovskite photovoltaics [2]. Previously, we reported an ALD-process for NiO based on bis-methylcyclopentadienyl-nickel as precursor and O_2-plasma as the co-reactant [3]. In this contribution, we investigate a thermal ALD process of NiO, with the motivation of expanding the ALD process capabilities on sensitive (e.g. to O_2 plasma) hybrid organic-inorganic chemistry substrates and offering opportunity for NiO process upscaling by spatial ALD, which is generally based on thermal processes.

For the present study, we selected (N,N'-di-tert-butylacetamidinato)Nickel(II) (Ni(^{t}Bu-MeAMD)$_2$) based on the relatively low melting point (87°C) with reasonable vapor pressure, and the availability of the precursor. Although literature addresses several thermal ALD processes of NiO based on Ni(^{t}Bu-MeAMD)$_2$ with reasonable growth rates [4,5], to our best knowledge, no saturation curves have been reported and only hot wall reactors were used so far. The decomposition temperature of the precursor (237°C), can limit the processing temperature, thereby suggesting the application of cold wall reactors. Hence, in this study, we use a cold wall reactor (FlexAL^{TM} MK1 Oxford Instruments).

We report saturation curves using Ni(^{t}Bu-MeAMD)$_2$ as the precursor and H_2O as the co-reactant resulting in a growth per cycle of 0.40-0.80 Å within a temperature window of 50-200°C. The process at ALD saturated condition also yields excellent uniformity (≥92% homogeneity over an 8 inch silicon wafer), with low impurity level in the film (3% C and 1% N), as observed by X-ray photoelectron spectroscopy (XPS). Rutherford backscattering spectroscopy analysis confirms a nearly stoichiometric film of O:Ni = 1.1 (deposition at 150°C). XPS also reveals the presence of oxide and (oxy)hydroxide terminal groups indicating the presence of both Ni^{2+} and Ni^{3+} oxidation states, imparting the p-type character to the film, key for selective hole transport behavior. Moreover, X-Ray diffraction data show a preferred orientation in the (111) direction for the film as opposed to (200) earlier observed in plasma-assisted ALD NiO, and beneficial for the O_2 evolution reaction in water-splitting [1].

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