Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+EM+PS+TF-TuM

Area Selective Processing and Patterning

Moderators: Prof. Dr. Greg Parsons, North Carolina State University, **Dr. Silvia Armini**, IMEC, Belgium

8:00am **AP+EL+EM+PS+TF-TuM-1 ASCEND: A Novel Solution-Based Method To Control Deposit Composition and Placement**, *Jevalyne Vienes,* ***Amy Walker,*** University of Texas at Dallas

We introduce a novel selective deposition process called ASCEND, or "Additive and Surface Control of Electroless Nanostructure Deposition." ASCEND integrates mechanistically-informed and well-controlled extensions of electroless deposition (ELD) and chemical bath deposition (CBD). It uses hybrid ELD-CBD conditions and patterned surfaces to deposit strongly adherent metallic and metal chalcogenide films and nanowires. It is inexpensive, easily scaled, and compatible with technologically relevant substrates. We illustrate ASCEND using Cu and CuS deposition. First, we employ ethanolamine additives in Cu ELD using dimethylamine borane (DMAB) on –OH and $–CH_3$ terminated alkanethiolate self-assembled monolayers (SAMs) either to deposit nanowires or perform area-selective deposition. Using monoethanolamine or triethanolamine copper nanowires are formed at the junction of patterned –OH/$–CH_3$ terminated SAMs. In contrast using diethanolamine, area selective deposition is observed in the $–CH_3$ terminated SAM area. Using TOF SIMS data we show that monoethanolamine and triethanolamine adsorb vertically (or at an angle) with the amine group interacting with the $–CH_3$ terminated SAM and leaving the hydroxyl groups free to interact with the bath components. This causes repulsion of the DMAB reducing agent, hindering deposition on the $–CH_3$ terminated SAM areas leading to nanowire formation. In contrast, diethanolamine adsorbs flat on $–CH_3$ terminated SAMs and no nanowire formation is observed; rather area-selective deposition occurs.

In the second experiment we control the deposit composition in Cu ELD using thiourea, which is a common bath additive, on -OH, -COOH and $–CH_3$terminated SAMs. At < 10^{-2} M thiourea, Cu films are deposited on all substrates. At ≥ 10^{-2} M the deposited layers are copper sulfides. At pH 5 and pH 9, the film is composed of CuS for all functionalized SAMs studied, while at pH 12 the deposit is Cu_2S. We attribute this to the role of thiourea in the bath. At low concentrations, thiourea acts as a complexing and reducing agent, while at high concentrations (> 10^{-2} M) the dominant reaction is thiourea hydrolysis leading to the formation of copper sulfides. Finally, exploiting this understanding we demonstrate a simple method to deposit layered Cu/Cu_xS and CuS nanowires on patterned SAM substrates by changing the TU concentration in the bath.

8:15am **AP+EL+EM+PS+TF-TuM-2 Using Acetylacetates to Control Chemical Reactivity and Physical Properties of Surfaces**, ***Andrew Teplyakov,*** University of Delaware

Over the last few years, the applications of various acetyl acetates in tuning both chemical reactivity of surfaces in deposition and etching processes and physical properties of the interfaces and thin films have received a substantial attention both from fundamental perspective and from applications point of view. This presentation will analyze the chemistry of several acetylacetates, including the ligands formed on surfaces by acetylacetone (acacH), hexafluoroacetylacetone (hfacH) and 1,1,1-trifluoroacetylacetone (tfacH) and the implications of this chemistry in area-selective atomic layer deposition (AS-ALD), atomic layer etching (ALE), and tuning optoelectronic properties of oxide surfaces and thin films. The effects of the gas-phase keto-enol equilibrium and the acid/base properties of oxide surfaces on the adsorption mechanisms will be discussed. The applications of this knowledge to design non-growth and growth surfaces for ALD and to propose new chemistries for ALE of 2D materials will be demonstrated.

8:30am **AP+EL+EM+PS+TF-TuM-3 Atomic Layer Etching for Advanced Logic Devices**, ***Masanaga Fukasawa,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

The dimensions of advanced logic devices require atomic-level control of variability, and atomic-layer etching (ALE) is a promising technique to meet this requirement. By separating adsorption and desorption, ALE improves controllability compared with conventional RIE. Currently, however, the long process time—leading to increased manufacturing cost—remains a major challenge, and thus industrial adoption has been limited. Nevertheless, in next-generation highly scaled 3D transistors such as CFETs, further improvements in etch selectivity, mitigation of pattern loading, and reduction of etch-induced damage are required. As a result, the importance of ALE is expected to increase [1].

To further improve etch selectivity, we have developed a technique that integrates area-selective deposition (ASD) and ALE within a single etching chamber to achieve ultra-high etch selectivity [2]. In atomic-scale processes such as ALD and ALE, understanding surface reactions and process performance at the atomic level enables more precise process design through the combination of individual reaction steps. Moreover, this approach is beginning to be adopted not only for ASD + ALE but also for ASD + RIE [3] in various process modules. In particular, with High-NA EUV lithography reducing resist thicknesses to below 30 nm, extremely high etch selectivity becomes even more critical. Thus, integration schemes that combine ASD with RIE/ALE will play an increasingly important role.

Regarding low-damage processing, although several studies have reported blanket-level evaluations, examples that demonstrate practical-level performance have been limited. In this work, we applied ALE or RIE to the bottom-break step of contact hole etching and compared the resulting electrical characteristics of contact chains. The results clearly show that ALE provides superior performance [4].

ALE delivers the controllability, reproducibility, and integrability required for next-generation semiconductor technologies, and elevates semiconductor fabrication to a new level of precision. I believe ALE will become increasingly essential in advanced logic device manufacturing.

Acknowledgement: This paper is based on results obtained from the project, "Research and Development Project of the Enhanced Infrastructures for Post-5G Information and Communication Systems" (JPNP20017), subsidized by New Energy and Industrial Technology Development Organization (NEDO).

[1] M Honda *et al., J. Phys. D: Appl. Phys*. **50**, 234002 (2017). [2] M. Fukasawa *et al., JJAP.* **64,** 06SP17 (2025).

[3] M. Matsui *et al., JVST A* **41**, 063002 (2023). [4] A. Hirata *et al., Proc. of IEEE IITC (*2026), San Jose, accepted for oral presentation.

9:00am **AP+EL+EM+PS+TF-TuM-5 Band Practice: Tuning Gold's Workfunction Through NHC d-Band Interactions**, ***Sean Barry,*** Carleton University, Canada*; Wai Tung Shiu, Paul Ragogna,* Western University, Canada

N-heterocyclic carbenes (NHCs) have emerged as robust small-molecule inhibitors (SMIs) for modifying metal surfaces, yet a quantitative understanding of their influence on surface electronic structure remains limited. Here, we investigate the modulation of the d-band center of a gold surface by NHC adsorption using a combination of solution- and vapour-phase deposition. Four structurally distinct NHCs were deposited on Au substrates, and the resulting interfaces were characterized using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

All NHCs formed stable monolayers on Au, with surface coverages that depended on both molecular structure and deposition method, ranging from 1.88 to 3.56 NHC/nm^2. UPS measurements revealed significant reductions in the Au work function (up to ~1.2 eV), with vapour-deposited films exhibiting larger shifts, consistent with differences in interfacial structure and electron redistribution. Analysis of the valence band spectra shows a systematic lowering of the Au d-band center upon NHC adsorption, indicating increased filling of antibonding states and weakened adsorbate–metal interactions.

Three primary factors governing d-band modulation were molecular orientation and the formation of $Au(NHC)_2$ adatom complexes, which lead to enhanced electron donation. Surface coverage plays a critical role, with higher coverages producing stronger modulation due to increased adsorbate–metal interactions. Finally, ligand electronics, particularly backbone substitution, influence the NHC's σ-donating ability and thus the extent of electronic perturbation at the interface.

This presentation will discuss the structure-function relationships of NHC substitution and coverage as well as absorption interactions.

9:15am **AP+EL+EM+PS+TF-TuM-6 Inhibition of SiO_2 by plasma treatments for bottom-up gap-fill applications**, ***Aurelia Trevisan,*** *Adrie Mackus, Erwin Kessels,* Eindhoven University of Technology, The Netherlands

As the features in electronic devices become smaller, top-down processes based on lithography need eventually to be complemented by bottom-up processes such area selective atomic layer deposition (AS-ALD). Although

ALD allows for conformal deposition on 3D features, it is challenging to fill high aspect ratio (AR) trenches without the formation of defects such as voids and seams in the middle. To obtain a defectless bottom-up gap-fill of a trench by ALD, the growth per cycle (GPC) of the employed ALD process should be lower at the top of the trenches than at the bottom. Different approaches that result in a decreased GPC on the top of AR trenches for seamless gap-fill have been studied employing molecular inhibition species[1] and NH_3 plasma pre-treatments.[2]

In this work, we investigated the mechanisms of inhibition of SiO_2 by NH_3, N_2/H_2 and SF_6/H_2 plasma exposures aiming at the application of such plasma pre-treatment for achieving gap-fill with SiO_2. We exposed the SiO_2 surface to NH_3, N_2/H_2 and SF_6/H_2 plasma at different conditions and we studied the surface chemistry by reflection-absorption infrared spectroscopy (RAIRS). For a NH_3 plasma exposure, we found that the substitution of the OH groups with NH_2 groups is almost complete[3] at low NH_3 pressure from the comparison of the areas of the OH peak (~3740 cm^{-1}) in the RAIRS spectra acquired after the plasma exposures at different NH_3 pressures. Next, to investigate the inhibition of the SiO_2 surface by plasma, RAIRS spectra were also obtained after dosing the Si precursor, bis(diethylamino)silane (BDEAS), with and without the plasma treatment step. From the IR spectra, we found that the amount of adsorbed BDEAS molecules on SiO_2 pre-treated with NH_3 plasma (60s, 0.01 mbar) is reduced by ~82%.

A NH_3 plasma pre-treatment was added before the dose of the precursor to every cycle of the SiO_2 PE-ALD process. The effect of the NH_3 plasma pre-treatment on the growth was investigated by conducting spectroscopic ellipsometry (SE) after every cycle. When the NH_3 plasma pre-treatment was added, a 53% reduction of the GPC was obtained. We expect this reduction to be enough to achieve gap-fill of high AR trenches, which will be studied by cross-sectional transmission electron microscopy.

References

[1] C. T. Nguyen *et al., Nature Communications* **13**, 7597 (2022)

[2] Y. Choi *et al.*, *Scientific Reports* **12**, 15756 (2022)

[3] L. T. Zhuravlev, *Colloids and Surfaces A: Physiochemical and Engineering Aspects* **173**, 1-38 (2000)

9:30am **AP+EL+EM+PS+TF-TuM-7 Precursor Isomerization-Enabled Etching Amplification: A Novel Route to Area Selective Deposition of SiOC Films**, ***Xiaocheng Huang**, Junjie Zhao,* Zhejiang University, China

Self-aligned patterning via area selective deposition (ASD) is a promising approach to mitigate overlay variations challenges in photolithography for advanced nanomanufacturing. However, it remains difficult to achieve area selective deposition when the adsorption and/or film growth on the target non-growth surface (NGS) exceeds that on the target growth surface (GS). We developed an etching amplification strategy based on precursor isomerization for selective deposition of SiOC when adsorption and/or film growth was higher on the target NGS than on the target GS. *In-situ* DRIFTS demonstrated that V_3D_3 cyclosiloxane undergoes ring-opening on CoO_x surfaces. This ring-opening reaction significantly enhances the etching rate under O_2/Ar plasma by 243% compared to the pristine pV_3D_3, as confirmed by *in-situ* QCM measurements. *In-situ* QCM during ASD cycles showed higher mass gain on CoO_x than on SiO_2 during V_3D_3 deposition steps; however, the subsequent etching step completely removed the adsorbed species from the NGS due to etching amplification. By integrating deposition and etching processes, we achieved selective deposition of a ca. 18.36 nm thick SiOC film on pre-patterned Co/SiO_2 substrates with nearly 100% selectivity. This work sheds light upon etching amplification by precursor isomerization for developing highly selective ASD processes.

9:45am **AP+EL+EM+PS+TF-TuM-8 A Novel Hybrid Approach to Area-Selective Deposition: Combining Two Strategies for Blocking Growth**, *Jay Swarup, James Jensen, Gokul Rajagopal, **James Engstrom**,* Cornell University

Area-selective atomic layer deposition (AS-ALD) has emerged as a promising bottom-up nanofabrication strategy for next-generation semiconductor manufacturing, where continued device scaling makes conventional lithographic patterning increasingly difficult and costly. Selectivity can be achieved by passivating non-growth surfaces (NGS) with blocking molecules while permitting growth on designated growth surfaces (GS), and it depends critically on precursor chemistry, blocking molecule identity and application method, and reactor temperature. Here we systematically investigate two blocking strategies for AS-ALD of Al_2O_3 targeting selective growth on Cu (GS) with suppression on SiO_2 (NGS) using BDMADA-Al, a bulky, non-pyrophoric precursor [1]. We employ *in situ* real time quartz crystal microbalance (QCM) techniques, coupled with selected *ex situ* techniques including X-ray photoelectron spectroscopy (XPS).The first strategy employs sequential dosing of a small molecule, while the second strategy introduces a co-adsorbate dosed simultaneously with the precursor to enable competitive adsorption at NGS reactive sites. In the first strategy, dimethylamido trimethylsilane (DMATMS) was applied repetitively in an ABC-type cycle (T = 285 °C), which produced modest blocking efficacy, where detectable growth from QCM could be delayed for the first ~ 20 cycles, while Al is clearly observed with XPS after 40 cycles.In the second strategy we also employ an ABC-type cycle, but also introduce a co-adsorbate dosed simultaneously with BDMADA-Al at T = 120 °C.We examined six different co-adsorbates, all possessing reactive functional groups, which revealed stark differences in blocking efficacy depending on the co-adsorbate used.Three co-adsorbates did not enhance blocking but, rather, produced linear (with exposure time) CVD-like growth during the combined precursor/co-adsorbate pulse.In contrast, three co-adsorbates yielded *complete blocking* of growth on SiO_2 for at least 40 cycles of ALD, confirmed by both QCM and XPS.In order to verify the operative mechanism of competitive adsorption we varied both the partial pressure of the co-adsorbate and the reactor temperature.We found that by either decreasing the partial pressure of the co-adsorbate, or increasing the temperature led to less effective blocking of growth, confirming the mechanism based on competitive adsorption.These results demonstrate that an approach that combines two strategies can produce synergy and a more effective method to enable area selective deposition.

[1]J. V. Swarup, H.-R. Chuang, J. T. Jensen, J. Gao, A. L. You and J. R. Engstrom, J. Vac. Sci. Technol. A **43**, 022404 (2025).

11:00am **AP+EL+EM+PS+TF-TuM-13 Probing Reactivity at Heterointerfacial Sites Using Area Selective Atomic Layer Deposition**, *Shani Monadeev, **Oz M. Gazit**, Alexander Stook,* Technion Israel Institute of Technology, Israel

Background

Heterointerfaces are a sub-class of defects arising from atomic mismatches across material boundaries. These coordinatively unsaturated sites modulate the electronic and geometric structure of catalysts to facilitate specific reactive adsorption, activation, and transformation of reactant molecules.[1] In electronic devices the critical heterointerfaces are “buried” between the layers,[2] whereas for catalysts, the reaction performance can depend on both the buried interfaces (i.e. metal support interactions) and on the exposed heterointerfacial (defect) sites, interacting with substrate and product molecules, see **Scheme 1**.

Results and discussion

In the current work, we use a bottom-up area selective atomic layer deposition (AS-ALD) to form supported thin layer raft-like oxides. To facilitate the AS geometry, we developed a new approach, which uses NaCl nanocrystals as masking domains during the ALD process. This unique approach allows us to apply this methodology onto silicon wafers and on different surface area particulate silica support materials. The HRSEM-EDS (Energy Dispersive Spectroscopy) mapping in **Figure 1** shows an example of a well-defined multilayer structure, formed following the sequential deposition of TiO_2 (≈20 nm) and subsequently Al_2O_3 (≈20 nm) layers onto an NaCl-mask before and after mask removal. Leveraging on the strength of AS-ALD we study the structure, binding energy, strain and more of the exposed heterointerface, aiming to decuple those from the exposed basal plan and bulk effects. We compare our AS-ALD materials to materials obtained using a top-down deposition of thin nanosheets of layer double hydroxides. All materials are extensively characterized using XPS, DRIFT-IR, HRSEM and HRTEM, grazing angle-WAXS and probe molecules TPD-MS. The functionality of the heterointerfacial sites is tested using Aldol type condensation reactions for the conversion of biomass derived platform molecules as a target and probe reaction.

References

(1)Xie, C., et al., ACS Catal. 2020, 10 (19).

(2)Christensen, D. V., et al., APL Materials 2018, 7 (1), 013101.

11:15am **AP+EL+EM+PS+TF-TuM-14 Area-selective Atomic Layer Deposition of Al2O3 on SiNx with Aminosilane-Functionalized SiO2 as the Nongrowth Surface**, ***Andrew Kaye**,* Colorado School of Mines*; Bhushan Zopé,* Intermolecular, Inc.*; Xinjian Lei, Ronald Pearlstein, Haripin Chandra, Agnes Derecskei,* EMD Electronics*; Sumit Agarwal,* Colorado School of Mines

SiO_2 and SiN_x are two of the most extensively used dielectric materials in semiconductor manufacturing. Previously, we showed that area-selective ALD of Al_2O_3 can be achieved on SiN_x by passivating the SiO_2 surface with

aminosilanes. Using *in situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy (see Figure 1), we will show that the aminosilanes react with both the SiO_2 and SiN_x surfaces, but the coverage of aminosilanes on the SiN_x surface is incomplete, which does not prevent ALD of Al_2O_3 from dimethylaluminum isopropoxide (DMAI) and H_2O, but simply introduces a nucleation delay of 5-10 cycles. However, selective growth of Al_2O_3 on SiN_x was limited to ~1 nm at which point DMAI started to react with the SiO_2 surface to nucleate film growth.

Based on these initial studies, our hypothesis was that there are residual Si–OH groups that remain on the SiO_2 surface react with DMAI to initiate growth of Al_2O_3. We have also shown that DMAI likely coordinates with Si–O–Si groups on aminosilane-functionalized SiO_2 films, which also leads to nucleation; therefore, simply reducing the surface Si–OH group density is inadequate. To extend the nucleation delay on SiO_2, we created a set of plasma-deposited SiO_2 surfaces with a controlled density of surface Si–OH groups by first preheating from the deposition temperature of 150 °C up to 500 °C, and then by cooling the substrate to a lower temperature prior to ALD of Al_2O_3. We used aminosilanes with different size head groups to study the uptake of aminosilanes and the steric blocking effects of both Si–OH and Si–O–Si sites to block Al_2O_3 ALD. The headgroup size did not significantly impact the initial uptake of aminosilanes with the same size leaving groups (see Figure 2). Using *in situ* ellipsometry, we show that aminosilanes with larger head groups resulted in more selective growth on SiN_x over SiO_2. Next, we showed that increasing the aminosilane dose increased the nucleation delay of Al_2O_3 ALD on both SiO_2 and SiN_x surfaces due to increased coverage, but selectivity did not improve significantly. Finally, we show that using a two-step aminosilane passivation scheme with sub-saturation doses of a large aminosilane and then a small aminosilane resulted in >3 nm of selective Al_2O_3 ALD on SiN_x over SiO_2 surfaces (see Figure 3).

11:30am **AP+EL+EM+PS+TF-TuM-15 Beyond Two-Color Selectivity: Area Selective Deposition on Multi-Oxide Surfaces Using Small Molecules Inhibitors***, **Benjamin Sanhueza,** Marc J. M. Merkx, Wilhelmus M. M. Kessels,* Eindhoven University of Technology, Netherlands*; Tania E. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; Adriaan J.M. Mackus,* Eindhoven University of Technology, Netherlands

Area-selective deposition (ASD) using small molecule inhibitors (SMIs) emerges as a promising bottom-up alternative, enabling selective deposition on growth areas (GAs) while inhibiting the non-growth areas (NGAs). Although ASD has shown strong potential, most studies are limited to two-surface-selectivity, which does not capture the multi-material complexity of modern semiconductor devices.[1]. In this context, we investigate the selectivity of SiO_2 ASD in a multi-oxide system by evaluating the role of different SMIs and their impact on inhibition selectivity, with relevance on 3D memory [2] and 3D logic devices.[3]

Here, we employ a previously developed SiO_2 ASD process on Al_2O_3 and SiO_2 surfaces,[4] using the bis(diethylamino)silane (BDEAS) precursor, H_2 and O_2 plasma as co-reactants, and different SMIs. Building on this process, we investigate multi-surface selectivity by introducing ZrO_2 as an additional third oxide surface.

Among the SMIs investigated, acetylacetone (Hacac) is presented as a representative case. *In situ* reflection–absorption infrared spectroscopy (RAIRS) shows that Hacac reacts with ZrO_2, achieving surface saturation and up to 96% blocking of a single BDEAS dose, which is comparable to that observed on Al_2O_3 as an NGA. Preliminary results further indicate that the H_2 plasma pre-treatment increases the density of isolated and vicinal –OH groups, enhancing Hacac coverage and improving blocking up to 99.5%, demonstrating the strong influence of this plasma pre-treatment on the ZrO_2 surface.

In situ ellipsometry measurements show that ZrO_2 acts as an effective NGA, exhibiting a nucleation delay of up to 28 cycles (~2.6 nm of selective SiO_2 deposition). Remarkably, similar selectivity is achieved on both Al_2O_3 and ZrO_2 surfaces, indicating consistent inhibition behavior across different oxides.[1], [5]

In addition to the results of this case study, it will be discussed that the choice of SMIs can tune inhibition behavior enabling different growth across surfaces. In this way, the loss of selectivity can be preferentially initiated on one NGA prior to another through SMI selection, enabling controlled thickness variations across different materials.

References

[1]: Lee et al., *Chem. Mater.* 37 (2025) 1741–1758.

[2]: Kim et al., *Curr. Appl. Phys.* 64 (2024) 8–15.

[3]: Wang, *Micromachines* 15 (2) (2024) 269

[4]: Yu et al., *Appl. Surf. Sci.* 665 (2024) 160141

[5]: Thelven et al., *Adv. Mater. Technol.* 10 (2025), e00284.

11:45am **AP+EL+EM+PS+TF-TuM-16 Surface Hydroxyl Topology and Relative Orientation Effects on Surface-Inhibitor Reactivity: Revisiting Chemical Passivation in Alumina and Zirconia.***, Lucas Lodeiro, Nicolás Rozas-Castro,* Universidad Tecnica Federico Santa Maria, Chile*; Dennis Hausmann, Rachel Nye de Castro,* Lam Research Corporation*; Adriaan Mackus,* Eindhoven University of Technology, Netherlands*; **Tania Sandoval,*** Universidad Tecnica Federico Santa Maria, Chile

Hydroxylated metal oxide surfaces are paramount for catalysis and thin–film processing. In this context the reduction of surface reactivity via molecular inhibitors or chemical passivation is a common and necessary practice. Small–molecule inhibitors (SMIs) such as acetylacetone (Hacac) and acetic acid (HAc) are widely employed to inhibit growth by reactive site consumption on hydroxylated oxides.[1] Despite their ubiquitousness, the influence of **surface site configuration** on inhibitor reactivity remains unexplored.

Experimental evidence that chemically distinct hydroxyl motifs exhibit different reactivities toward SMIs is available.[2] In this work, we revisit the chemical passivation of hydroxylated alumina and zirconia by SMIs, with emphasis on the role of surface site configuration, defined as a combination of Local Topology and Relative Orientation of hydroxyl groups on metal oxide surfaces. Rather than treating hydroxylated sites as a whole entity, we examine how geometrically and electronically distinct surface motifs modulate inhibitor binding modes and reactivity.

Considering that systematic exploration of all possible site configurations rapidly becomes challenging due to the large chemical space, we further investigate whether simple surface descriptors, derived from local electronic structure and geometry, can provide predictive insight into surface reactivity toward SMIs. Our goal is to identify descriptor trends (e.g., charge distribution, coordination, or accessibility metrics) that correlate with inhibitor adsorption behavior, enabling informed prioritization of surface motifs prior to exhaustive site screening.

By linking surface site configuration, inhibitor-surface reactivity and descriptor–based analysis, this work aims to understand the nuances in the chemical passivation of metal oxide surfaces, and provides guidance to design descriptor–informed screening strategies.

[1] Chem. Mater. 2020, 32, 3335–3345

[2] J. Phys. Chem. C, 2022, 126, 4845–4853

12:00pm **AP+EL+EM+PS+TF-TuM-17 Can pFA Invert Selectivity? The Chemistry of TiO_2 Nucleation on Chlorinated and Aminated Si(111) Surfaces During Thermal Atomic Layer Deposition***, **Tyler Parke,** Andrew Teplyakov,* University of Delaware

Recently, the near-atomic level precision offered by atomic layer deposition (ALD) has been exploited by developing area-selective schemes which can be used to fabricate complex three-dimensional nanostructures, such as modification of a substrate's surface functionality to induce a "selectivity inversion" between growth surfaces (GS) and non-growth surfaces (NGS). This is a newly developing technique, which has only been demonstrated thus far with few vapor-phase treatments, and which requires a molecular level understanding of the chemistry between surface and modifying reactant, as well as between modified surface and precursor. Here, single-crystal Si(111) surfaces terminated with hydrogen [H-Si(111)] or chlorine [Cl-Si(111)] monolayers, which are typically NGS's in thermal TiO_2 processes, are proposed as potential substrates to modify with a basic amine, para-fluoroaniline (pFA), and invert their selectivity. Amination with pFA is demonstrated to selectively modify the H-Si(111). Thermal TiO_2 ALD is subsequently attempted to test the aminated surface's capability as a GS or NGS. The fundamental chemistry of the interaction between the pFA and either surface, as well as between the aminated surface and ALD precursors $TiCl_4$ and tetrakis(dimethylamido)titanium (TDMAT), are probed with a combination of X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), density functional theory (DFT), and time of flight secondary ion mass spectrometry (ToF-SIMS) in order to determine the structure of the aminated surface and understand its effect on reactivity under ALD conditions.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP1+EL+MS+PS+TF-TuA

Advanced Atomic Scale Processing through Modeling and Simulation

Moderators: Prof. Dr. David Graves, Princeton University, **Prof. Dr. Satoshi Hamaguchi**, Osaka University, Japan

2:15pm **AP1+EL+MS+PS+TF-TuA-1 Design and performance of AI agents interfacing with atomic layer deposition tools**, ***Angel Yanguas-Gil,*** Argonne National Laboratory **INVITED**

In recent years there has been an increased interest in exploring the integration of generative AI in combination with experimental tools to create multipurpose autonomous systems that can solve complex research problems. This vision relies on AI agents based on LLMs that can autonomously interact with experiments to solve multiple tasks (e.g. "Grow 20 nm of tin oxide" or "selectively grow 10 nm of Cu on Co but not on silicon oxide"). However, in order to be useful, these systems have to be compatible with state of the art manufacturing tools and they have to perform reliably well in a broad enough set of materials synthesis tasks.

In this presentation, I will focus on these two aspects in the context of atomic scale processing. First, I will describe how we have augmented an existing ALD tool so that it can be integrated with generative AI models. Our approach relies on defining a Python interface and API that abstract all the specific details of the hardware from the AI agent, while making it compatible with standard approaches for tool use with LLMs. I will also describe how we have implemented AI agents that can communicate with this ALD tool as well as with existing data, such as data logs and background data on ALD and area selective deposition.

In the second part of the presentation, I will introduce a general methodology to evaluate the performance of AI agents on atomic scale processing tasks. We have applied it to evaluate the performance of state of the art models in instruction, process discovery, and materials discovery challenges in the context of atomic scale processing, primarily ALD and selective growth. In all these cases the output of the challenge is a specific instruction to run one or more processes in an ALD tool. Our results show that state of the art models excel at instruction tasks, but they struggle on process and materials discovery tasks where they involve processes and materials that are underrepresented in the literature, pointing to potential limitations and areas of improvement for for future AI models specialized in materials synthesis and atomic scale processing.

This research is based upon work supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357.

2:45pm **AP1+EL+MS+PS+TF-TuA-3 A Multiscale Framework for ALD/ALE Process and Precursor Development Using Neural-Network-Potential Atomistic Simulations and COSMO-SAC Thermodynamic Modeling**, ***Yukihiro Shimogaki,*** The University of Tokyo, Japan

Atomic layer deposition (ALD) is indispensable for gate-all-around transistors, high-aspect-ratio DRAM capacitors, and 3D NAND, where conformality and precise thickness control are both required. Atomic layer etching (ALE), the reverse of ALD, matters for low-damage, selective integration, while area-selective deposition (ASD) is attractive but suffers "selectivity loss": unwanted nuclei form on non-growth areas and degrade selectivity over time. We present a multiscale framework coupling COSMO-SAC thermodynamic modeling for precursor down-selection with neural-network-potential (NNP) atomistic simulations for reaction-mechanism analysis; an integrated ALD+ALE scheme designed within it enables highly selective, robust ASD.

An ideal precursor reaches saturation adsorption and is delivered stably; a vapor pressure >=100 Pa below 100 C, preferably ~1000 Pa, broadens the process window. Conventional COSMO-SAC is often inaccurate for metal-containing organometallics. By tuning dispersion-related parameters we obtained good agreement between predicted and measured vapor pressures, enabling efficient down-selection. For Co precursors the framework predicted a high vapor pressure for CpCoCOTFE; the synthesized compound showed ~1060 Pa at 85 C. The same volatility prediction directly guides ALE, where formation and removal of volatile products are central.

Surface-reaction analysis has long been limited by the cost of reaction-path and vibrational searches. NNP-based simulations (e.g., Matlantis) now provide near-DFT accuracy at large scale, making ALD/ALE surface mechanisms tractable. For the Co precursor, NNP indicated that controlling surface hydrogen coverage prior to dosing suppresses carbon incorporation from side reactions; this was confirmed experimentally, showing precursor design (vapor pressure) and reaction design (surface state) must be co-optimized.

For ASD with CCTBA, NNP molecular dynamics showed facile reaction on Cu but low reactivity on SiO_2, and selective growth on Cu was experimentally confirmed. Residual Co nuclei on SiO_2 degrade selectivity; we designed an ALE path in which Co is chlorinated by SO_2Cl_2 and reacts with Hfac to form volatile products whose volatility is supported by COSMO-SAC. The resulting ALD (growth) + ALE (nuclei removal) scheme restores robust selectivity. Finally, sub-monolayer growth per cycle (~0.1 ML) is rationalized by steric hindrance, and NNP-MD with kinetic Monte Carlo captures these collective adsorption dynamics. This COSMO-SAC + NNP framework offers a unified route to co-develop ALD/ALE processes (Atomic Layer Process, ALP) and precursors and to overcome ASD selectivity loss.

3:00pm **AP1+EL+MS+PS+TF-TuA-4 Re-designing ALD Experiments for AI-ready Data: The IGZO Case Study**, ***Eleni Poupaki,*** *Cas Visser, Freek Klabbers, Adrie Mackus, Erwin Kessels,* Eindhoven University of Technology, The Netherlands

The AtomicLimits ALD database [1] is a community-driven repository of ALD processes from the literature. The next step is to populate it with more data suitable for artificial intelligence (AI) and machine learning (ML) models. [2] Recent efforts have used large language models for structured data extraction from publications. [3] However, literature data remains fundamentally limited for data-driven modeling: it is incomplete, often missing key process parameters, biased toward successful experiments, and inconsistently reported. ML can accelerate ALD development by predicting film properties, guiding experiment design, and identifying optimal recipes. Unlocking this potential requires not only more data, but experiments designed to produce data suitable for ML. We address this challenge using ALD of InGaZnO (IGZO) as a case study. IGZO is a quaternary oxide semiconductor that has emerged as an alternative to crystalline silicon channels, used in displays and increasingly explored for DRAM. Amorphous IGZO exhibits high electron mobility, ultralow leakage, and a low thermal budget. [4,5] ALD is well-suited for IGZO, due to its sequential, self-limiting surface reactions, enabling precise control of thickness and composition. [6] For multicomponent materials like IGZO, composition is controlled via the supercycle approach, with subcycles of In_2O_3, Ga_2O_3, and ZnO. Their relative ratios and sequence strongly influence the resulting film properties [7], creating a vast, interdependent parameter space. In this work, we develop a protocol for generating AI-ready ALD experimental data, demonstrated on IGZO. The protocol proceeds stepwise from binary to ternary to quaternary processes, with explicit criteria at each stage: binary processes are characterized for saturation and nucleation, and the ternaries (GaZnO, InZnO, InGaO) are screened to identify supercycle criteria. Using these findings, we explore the supercycle parameter space, focusing on cycle ratio and mixing, with consistent characterization. We discuss preliminary trends in crystallinity and electrical properties across the explored space, contrasting with conventional optimization-driven experimentation. Finally, we outline how the resulting datasets enable ML-guided exploration of the IGZO supercycle space, paving the way toward AI-assisted ALD process optimization and a richer experimental foundation for community resources such as AtomicLimits.

[1] 10.6100/alddatabase

[2] Westermayr et al., Chem. Mater. 2026.

[3] Saddrudin, Poupaki et al., JVSTA 2026.

[4] Song et al., Nat. Electron. 2025.

[5] Okajima et al., IEDM 2025.

[6] Sheng et al., ACS AMI 2019.

[7] Oh et al., Ceram. Int. 2025.

3:15pm **AP1+EL+MS+PS+TF-TuA-5 Atomistic Modeling of Atomic Layer Etching and Deposition: HF/SiO2 ALE and TMA/Al2O3 ALD**, ***Fedor Goumans,*** Software for Chemistry & Materials, Netherlands

Atomic layer processes rely on surface reactions that are sequential, self-limiting, and highly sensitive to local chemical structure. Understanding these reactions at the atomistic level is essential for improving atomic layer deposition, atomic layer etching, and area-selective processing, but many key reaction steps occur at buried, transient, or chemically heterogeneous interfaces that are difficult to characterize directly. In this presentation, we

discuss how reactive atomistic simulations can support the interpretation and design of atomic layer processes, with examples from HF-based SiO_2 etching and TMA/Al_2O_3 deposition.

Reactive force fields and machine-learned interatomic potentials provide complementary routes for exploring surface chemistry over length and time scales beyond conventional first-principles molecular dynamics. Using these approaches, one can follow bond breaking and formation, surface hydroxylation, ligand exchange, fluorination, densification, and volatile product formation under process-relevant conditions. For SiO_2 etching, simulations can help identify how HF exposure modifies hydroxylated and strained oxide surfaces, how local bonding environments influence fluorination and material removal, and which surface motifs may control etch initiation. For Al_2O_3 deposition, simulations of TMA reactions with hydroxylated alumina surfaces can reveal the molecular origin of saturation behavior, steric effects, methane elimination, and the evolution of reactive surface sites across ALD cycles.

The broader goal is to connect the relevant calculated parameters such as sticking rate, thermal accommodation coefficients, and atomistic reaction mechanisms with experimentally observable trends in growth, etch rate, selectivity, and film quality. We highlight practical considerations for building reliable reactive models, including training data selection, validation against quantum chemical calculations, and the use of accelerated workflows. These examples illustrate how atomistic modeling can complement experiments by exposing reaction pathways, identifying limiting surface structures, and guiding the development of more predictive models for ALD and ALE process optimization.

4:00pm **AP1+EL+MS+PS+TF-TuA-8 Characterizing Directionality, Energy and Spatial Uniformity of Plasma Generated Neutral Beams for Low-Damage Material Processing**, ***Gonçalo A. Cardoso***, *Mark J. Kushner,* University of Michigan, Ann Arbor

Ion bombardment onto biased wafers during plasma etching can result in charge buildup within features that can deflect incoming ion trajectories, resulting in feature defects such as bowing or notching, or lead to device damage. UV photons emitted from the plasma might also cause surface defects such as dangling bonds [1]. These issues are exacerbated as device dimensions are scaled down, due to larger electric fields for a given charging potential and increased surface-to-volume ratio. This is particularly the case for the fabrication of 2-dimensional materials consisting of nearly monolayer thickness. Energetic neutral beams have been proposed as an alternative, low-damage and charge-free technique for etching and deposition, and particularly so for 2D materials. Such beams can be produced through ion acceleration and subsequent neutralization, either through charge-exchange collisions (volume neutralization) or by reflection from surfaces (surface neutralization) [2, 3]. The primary technical challenges for neutral beam sources involve optimization of directionality, energy and spatial uniformity of the energetic neutral fluxes striking the substrate.

In this paper, we discuss the results of a computational investigation of a neutral beam source consisting of an inductively coupled plasma separated from the wafer by a radio frequency (RF) biased grid powered at 10 MHz. Typical conditions for this source are pressures of tens of mTorr, gas mixtures containing Ar, O_2 and Cl_2 and biases on the grid of hundreds of volts. This source has been simulated using the Hybrid Plasma Equipment Model (HPEM).The Plasma Chemistry Monte Carlo Module (PCMCM) in the HPEM tracks the motion of ions (and neutrals) as they are accelerated by electric fields, collide with background gas particles and neutralize by reflecting from the grid. The PCMCM records the resulting neutral energy and angular distributions (NEADs) at the wafer. This work investigates the characteristics of these NEADs and how they are influenced by grid surface roughness (non-specular scattering), inelastic scattering from the grid, gas-phase charge-exchange reactions and pressure gradients across the grid.

This work was supported by the US Department of Energy, Office of Science, Fusion Energy Sciences (FES) and Basic Energy Sciences (BES) as part of the Extreme Lithography & Materials Innovation Center (ELMIC), a Microelectronics Science Research Center (MSRC), through the Plasma-enabled 2D Materials project (DEAC02-09CH11466); and by FES (SC-00274510).

4:15pm **AP1+EL+MS+PS+TF-TuA-9 Plasma Etching of Diamond: Molecular Dynamics Studies and Comparison to Experiments**, ***Louis Hoffenberg***, Princeton University; *Justin Boles,* University of Houston; *Jack Draney,* Princeton University; *Igor Kaganovich,* Princeton Plasma Physics Laboratory; *Vincent Donnelly,* University of Houston; *David Graves,* Princeton University

Nitrogen-vacancy (NV) centers in diamond are promising for multiple applications in quantum information processing and sensing, including in the fields of high-power/high-frequency electronics, quantum computing, and quantum sensing.[1] Diamond NV centers near surfaces can locally detect and measure physical quantities such as magnetic and electric fields with unprecedented sensitivity. However, these devices are currently limited by near-surface (<10 nm) defects that compromise charge stability and spin coherence.[2] Plasma etching of diamond has been widely employed to process and pattern diamond, but there is limited understanding of the mechanisms of plasma etching. In this work, classical molecular dynamics (MD) simulations are used to simulate O_2/Ar plasma etching of diamond, with comparisons to experiment. We explore both conventional reactive ion etching (RIE) and atomic layer etching (ALE) conditions. The experimentally validated MD simulations are used to identify fundamental etch mechanisms. Based on the MD simulations, we propose a parameterized reduced order model of diamond plasma etching that relates etch yield to ion flux, ion energy, and ion composition, as well as neutral O• radical to ion flux ratio.

References:

[1] Janitz et al. "Diamond surface engineering for molecular sensing with nitrogen-vacancy centers." J. Mat. Chem. C 10.37 (2022): 13533-13569.

[2] Sangtawesin et al. "Origins of diamond surface noise probed by correlating single-spin measurements with surface spectroscopy." Phys. Rev. X 9.3 (2019): 031052.

4:30pm **AP1+EL+MS+PS+TF-TuA-10 Predictive Screening of Sustainable Etchants via DFT Thermodynamics, Machine-Learned Vapour Pressures, and Infrared Spectra**, ***Christopher Pashartis***, *Philippe Bezard, Konstantina Philippidou, Geoffrey Pourtois,* IMEC Belgium; *Hideharu Shimizu, Yoshiki Nakoyama,* NSC, Belgium

Fluorinated etchants are heavily used in semiconductor processes for their high etch rates and material selectivity. Typical etchants such as CF_4 and c-C_4F_8 have global-warming potentials in the range of 7,400-13,900 over 100 years and atmospheric lifetimes exceeding hundreds of years, raising concern about the by-products of such processes. While abatement downstream is standard practice, it runs continuously and is never fully effective. Therefore, a more impactful path to reducing the climate footprint of fabrication is to identify replacement etchants that are intrinsically more sustainable while remaining competitive in performance.

Experimentally screening new etchants includes sourcing gases, fine-tuning reactor conditions, characterising effluent; it can be very slow and time consuming. We present a predictive screening workflow built on Density Functional Theory (DFT) rather than specialised plasma simulations: DFT-derived Gibbs free energies are used to solve the closed-system equilibrium for each etchant-substrate pair, giving both the predicted etch capability and the by-product distribution as a function of temperature, pressure, and stoichiometry. To translate predicted species into global warming potential, we couple this with two further ingredients: a graph neural network trained on open-source vapourpressure data to determine which by-products are most likely to be gaseous, and DFT-computed infrared spectra to estimate their radiative efficiency. We will present results aggregated across more than ten candidate etchants and three substrates (Si, SiO_2, Si_3N_4), demonstrating how the combined thermodynamics-volatility-impact screen can rank chemistries by their projected greenhousegas burden.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP2+EL+PS+TF-TuA

Advancing X-Ray Photoelectron Spectroscopy to enable Atomic Scale Processing

Moderators: Dr. Robert Bruce, IBM Research, T. J. Watson Research Center, **Dr. Eric Joseph**, IBM T.J. Watson Research Center

4:45pm **AP2+EL+PS+TF-TuA-11 Understanding the Chemical Reaction Mechanisms of Oxide, Nitride and Metal ALD: Insights from Operando X-Ray Photoelectron Spectroscopy***, **Joachim Schnadt,*** Lund University, Sweden **INVITED**

Over the past decades, atomic layer deposition (ALD) has emerged as a leading thin-film deposition technique, particularly within semiconductor technology. The reason is that ALD provides excellent thickness control down to the atomic scale, as a result of the use of sequences of self-limiting surface reactions. However, continued device miniaturization imposes more and more stringent demands on process control. Interfaces need to be engineered with extremely high precision, and lateral dimension control grows in importance. This implies that the exact surface chemistry underlying ALD – and this chemistry is both process and surface specific – needs to be understood in true detail. Experimental *operando* techniques provide an avenue towards the monitoring and characterization of the ALD surface chemistry in a time-resolved manner; these techniques can be applied during the deposition and at measurement rates that allow to resolve the time evolution of surface species and surface structure. Ambient pressure X-ray photoelectron spectroscopy (APXPS) is such an *operando* tool. In contrast to conventional X-ray photoelectron spectroscopy, it is carried out at pressures up to the millibar range, i.e. exactly the operational pressure regime of ALD. Time-resolved APXPS provides precise insight into the occurrence and time evolution of surface and subsurface species and their chemical state and provides information that can be used to formulate chemical reaction mechanisms in the different stages of deposition. In my presentation, I will discuss the capabilities of *operando* APXPS for research into ALD, using examples of research into the ALD of metal oxides and nitrides from transition metal amido or metal tetraisopropoxide complexes and water or ammonia. I will also highlight the first APXPS study into Pt metal ALD. Due attention will be given to instrumental aspects, foreseen future developments and a discussion of what can and what cannot be learned from APXPS.

5:15pm **AP2+EL+PS+TF-TuA-13 In vacuo XPS for Studying ALD Processes***, Matthias Minjauw, Tippi Verhelle, Jin Li, Jolien Dendooven,* ***Christophe Detavernier,*** Ghent University, Belgium **INVITED**

X-ray photoelectron spectroscopy (XPS) is a well-established technique for probing near-surface composition and chemistry. When employed as an in vacuo technique—i.e., without intermittent air exposure—it becomes a powerful tool for investigating surface chemistry during atomic layer deposition (ALD) processes. Three case studies will be presented: (1) the well-known TMA-based chemistry for ALD of alumina, (2) metal ALD with a focus on Pt growth (as reported by Li et al., J. Phys. Chem. C 2024, doi:10.1021/acs.jpcc.3c07568), and (3) ALD on lithium foil substrates (as reported by Verhelle et al., J. Mater. Chem. A 2026, doi:10.1039/D6TA00751A).

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+PS+TF-WeM

Thermal and Plasma Enhanced Atomic Layer Etching

Moderators: Dr. Eric A. Joseph, IBM Research Division, T.J. Watson Research Center, **Prof. Dr. Erwin Kessels**, Eindhoven University of Technology, the Netherlands

8:00am **AP+EL+PS+TF-WeM-1 Cyclic dielectric etching challenges for next-generation FDSOI logic and quantum devices**, ***François Boulard,*** CEA-LETI, France*; Ramy Ayoub,* CEA-LETI, France, Lebanon*; Emmanuel Petitprez, Stéphane Pocas, Nicolas Gauthier, Benoit Martin, Pierre Brianceau, Antoine Ronco,* CEA-LETI, France*; Bernard Pelissier,* LTM-CNRS, France*; Nicolas Posseme,* CEA-LETI, France **INVITED**

As logic devices dimensions scale down[(1)] and quantum gates advance in scalability and environment resilience[(2)], the demand for gentle, selective, and highly controlled fabrication processes has become critical. Atomic-scale processing—particularly cyclic approaches like Atomic Layer Etching (ALE) and quasi-ALE—has emerged as a potential solution. By leveraging fluorocarbon-based chemistries in sequential deposition/removal cycles, these methods have already demonstrated superior performances in terms of SiO_2 to Si_3N_4 selectivity, such as in Self-Aligned Contact (SAC) etching[(3)]. While the fundamental mechanisms of these cyclic processes are increasingly well understood[(4)], their industrial applicability—especially for advanced integration schemes—still faces challenges in versatility, robustness, and throughput. In this presentation, we will highlight recent advances in adapting cyclic etching strategies to selectively etch dielectric materials (SiO_2, SiON, Si_3N_4) for two cutting-edge applications: Contact multipatterning in next-generation FDSOI CMOS logic devices and intertwined gate patterning for cryogenic FDSOI quantum chips. This study explore the critical role of process parameters, including fluorocarbon precursor selection, multi-step cyclic strategies, substrate temperature and plasma power modulation, and their collective influence on etch per cycle stability, selectivity, uniformity, throughput, and pattern transfer fidelity.

By bridging fundamental insights with integration-driven optimization, this work clears the path to highly scalable, atomic-precision etching—a key enabler for both classical and quantum semiconductor technologies.

The research work presented in this paper was carried out in the framework of the FAMES Pilot Line of the Chips JU, funded by Horizon Europe grant 101182279 and the ANR NextGen project ANR-22-NEXTG001 of the France 2030 initiative. Part of this work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the “Recherche Technologique de Base” and "France 2030 - ANR-22-PEEL-0014" programs of the French National Research Agency (ANR).

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(2)B. Bertrand, et.al., International Electron Devices Meeting, IEDM 2023, DOI: 10.1109/IEDM45741.2023.10413763

(3)M. Honda, et.al, 2017, J. Phys. D: Appl. Phys. 50 234002 [tel:50 234002], https://doi.org/10.1088/1361-6463/aa6f27

(4)R.J. Gasvoda, J. Vac. Sci. Technol. A 38, 050803 (2020); https://doi.org/10.1116/6.0000395

8:30am **AP+EL+PS+TF-WeM-3 Atomic Layer Etching of TiN using O_2/Ar Plasma and SF_6/H_2/Ar Plasma Half-Cycles**, ***Kazuya Tajima,*** Hitachi High-Tech Corporation, Japan*; Andrew P. Kaye,* Colorado School of Mines*; Kazumasa Okuma, Hiroaki Ishimura,* Hitachi High-Tech Corporation, Japan*; Sumit Agarwal,* Colorado School of Mines

Titanium nitride (TiN) has become a widely adopted material for both logic and memory devices due to its appropriate work function with high-k gate stacks and excellent barrier properties against fluorine and oxygen diffusion. Atomic layer etching (ALE) of TiN was performed by a combination of surface modification by oxidation during the O_2/Ar plasma half-cycle and release of volatile etch products in the SF_6/H_2/Ar plasma half-cycle. [1,2] For the ALE experiments, we used low-resistivity TiN deposited by atomic layer deposition. In the O_2/Ar plasma half-cycle, TiN was oxidized to TiO_x with O radicals. For the SF_6/H_2/Ar plasma cycle, the SF_6-to-H_2 flow ratio was tuned to minimize continuous etching of TiN. Quadrupole mass spectrometry (QMS) was used to identify conditions that maximize the production of HF in the SF_6/H_2/Ar plasma, which acts as the etchant for surface modified TiO_x layer, and does not spontaneously etch TiN. Using QMS, we also identified the primary reaction products produced in each half-cycle. Our data show that NO was the primary nitrogen-containing product in the Ar/O_2 plasma half-cycle. TiF_2^+ and TiF^+ ions were detected by the QMS in the SF_6/H_2/Ar plasma half-cycle, which most likely originate due to cracking of TiF_4 parent molecules in the ionizer. The likely O-containing product during the SF_6/H_2/Ar plasma half-cycle is H_2O, which could not be detected due to the background signal in the QMS. In addition, we also detected SO^+ and SO_2^+ ions during both half-cycles due to the presence of S on the substrate and/or the chamber walls.

The etching process was performed at 200 °C. While the oxidation of TiN was quasi-self-limiting during the O_2/Ar plasma half-cycle, subsequent etching in the SF_6/H_2/Ar plasma half-cycle was not self-limiting. The synergy parameter, *S*, [3] is an indicator of the ideality of the ALE process. We show that the ALE end point could be determined by the time decay of the reaction products measured by the QMS, and the synergy parameter could be optimized by limiting the duration of the SF_6/H_2/Ar plasma half-cycle. We were able to obtain a synergy parameter of ~82% under optimized conditions.

[1]Lee et al., Chem. Mater. 29, 8202 (2017);

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[3] Kanarik et al.,J. Vac. Sci. Technol. A 35, 05C302 (2017);

8:45am **AP+EL+PS+TF-WeM-4 Atomic Layer Etch Process for InGaAs Using (CH4+H2)/Ar+ Plasma**, ***Burak Okur,*** *Ryan Walsh, J. Russell Renzas,* University of Nevada, Reno

Precise, damage-free etching of InGaAs with Angstrom-scale control is a critical requirement for next-generation III-V semiconductor device fabrication, including gate recess etching in InGaAs HEMTs, which require very precise etching of ~20 nm of InGaAs. Conventional plasma etching is insufficiently precise for this application and introduces subsurface damage and surface roughness, motivating the development of atomic layer etching (ALE) processes that achieve controlled material removal through sequential, self-limiting surface reactions.

In this work, we investigate a plasma-based ALE process for InGaAs using $(CH_4+H_2)/Ar^+$ chemistry, consisting of alternating surface modification and removal half-cycles. The expected volatile products are $In(CH_3)_3$, $Ga(CH_3)_3$, and AsH_3. The effects of chamber conditioning, process pressure, and Ar flow rate are systematically investigated to achieve self-limiting ALE behavior. Real-time optical emission spectroscopy (OES) measurements are used to monitor plasma species and investigate the role of residual CH-related species in the transition between self-limiting ALE and RIE-like behavior. For a process at 10 mTorr with 200 W ICP power, 5 sccm Ar, a 1 sec dose of 5 sccm CH_4 and 20 sccm H_2, and 5 sec etch time, an ALE window is present from 10-15 W RF bias, with EPC of 0.25 nm/cycle. The etched surfaces are characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM), and profilometry to evaluate etch per cycle (EPC), surface morphology, roughness evolution, and compositional uniformity of the InGaAs surface. Synergy is also measured.

9:00am **AP+EL+PS+TF-WeM-5 O2/CF4/Ar+ 3-Step Plasma Atomic Layer Etch Process for Aluminum**, ***Ryan Walsh,*** *Burak Okur, J. Russell Renzas,* University of Nevada, Reno

Aluminum is a light, conductive metal used in an incredible assortment of device fabrication processes, including in superconducting devices, where performance is highly sensitive to material impurities, interface damage, and critical dimensions. Most aluminum reactive ion etch processes use Cl_2 or BCl_3, which have the dual disadvantages of toxicity and post-etch corrosion. Fluorine is not typically used as an etchant for Al films because of the high melting point of AlF_3. It is known, however, that fluorinated AlO_x has a lower sputter threshold than untreated AlOx[1]. We present a novel 3-step plasma Atomic Layer Etch (ALE) process for Al using O_2, CF_4, and Ar^+. This room-temperature cyclical process starts by oxidizing Al in O_2 in Step A. Step B consists of a tetrafluoromethane dose to create an aluminum oxyfluoride modified layer. In Step C, this modified layer is removed via argon ion bombardment, using the oxide as an etch stop for the removal of the more easily sputtered oxyfluoride layer.

EPC of 0.08 nm/cycle and synergy of >99% were achieved with 100 W ICP power and 7 W table bias during step C. Etch control is governed by the thickness of the grown oxide and the depth of fluorine diffusion. We also present AFM, SEM, and XPS to show the effect of this process on the Al surface. This process could provide an avenue toward improved performance in aluminum-based superconducting devices.

[1] Chittock, N. J. (2024). Plasma processes for atomic layer etching. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Applied Physics and Science Education]. Eindhoven University of Technology.

9:15am **AP+EL+PS+TF-WeM-6 Directional Atomic Layer Etching of Lithium Niobate for Nonlinear Integrated Nanophotonics**, ***Ivy Chen,*** California Institute of Technology*; Frank Greer,* Jet Propulsion Laboratory (NASA/JPL)*; Austin Minnich,* California Institute of Technology

Atomic layer etching (ALE) is of intense interest in microelectronics, photonics, and other fields owing to increasing demands for nanofabrication with nanometer-scale precision, aspect-ratio independent etching, and sub-nanometer surface roughness. Nonlinear integrated nanophotonic devices typically employ complex oxides like lithium niobate for which dry etching processes perform poorly. Fundamental improvements in nanofabrication processes are vital to realize the full potential of nonlinear integrated nanophotonics for on-chip quantum information processing and beyond. Here, we report a directional ALE process for LN consisting of sequential exposures of HBr/BCl_3/Ar plasma for surface modification and Ar plasma for removal. We observe an etch rate of 1.04 ± 0.01 nm/cycle with a synergy of 84.6% at a temperature of 0°C. At higher process temperatures, the HBr chemistry is found to decrease redeposition compared to F- and Cl-based plasmas, which we attribute to the higher vapor pressures of Br-based products. A grating pattern etched entirely by the process (total etch depth of 220 nm) exhibits no aspect-ratio dependent etching (ARDE) down to the smallest tested gap of 150 nm, in contrast to ion milling in which ARDE manifests even at 300 nm gaps for the same etch depth. Additionally, we present results on applying our ALE processes to TFLN devices to obtain higher aspect ratios, smoother sidewalls, and precise etch depths, yielding enhanced performance metrics for coupler gratings, ring resonators, and spontaneous parametric downconverters for on-chip quantum information processing.

9:30am **AP+EL+PS+TF-WeM-7 Native Oxide Removal and Passivation of Niobium for Superconducting Devices**, ***Jessica Jones,*** Argonne National Laboratory*; Jeffrey Elam,* Argonne National Laboratory, USA

Superconducting materials are foundational to many quantum technologies, yet surface and interfacial disorder remain important barriers to device performance and scalability. In particular, native oxide formation on superconducting metals is believed to contribute to loss and decoherence, creating a need for processing methods that provide precise surface control while maintaining the integrity of the underlying material. Niobium is an attractive superconducting material because of its relatively high critical temperature and broad relevance to quantum circuit platforms. However, complex native oxide formation and near-surface chemical disorder complicate its integration into devices such as Josephson junctions and other superconducting circuit elements. Here, we investigate an atomic-scale surface treatment and passivation approach for niobium thin films aimed at improving control over the metal/oxide interface. Our results show that thermal atomic layer etching can effectively remove native surface oxides from niobium while preserving the underlying metallic surface. Subsequent atomic layer deposition prevents reformation of the native oxide layer on the surface. Together, these findings establish a promising pathway for interface control in superconducting niobium and support the development of improved fabrication strategies for quantum circuit technologies.

9:45am **AP+EL+PS+TF-WeM-8 Thermal Atomic Layer Etching of the Semiconductor Oxide Channel Materials by Sequential Surface Modification and Volatile Release Reactions**, ***Muhammad Hamza Ansar,*** *Steven George,* University of Colorado Boulder

Indium gallium oxide (IGO) and Indium gallium zinc oxide (IGZO) can be used as channel materials in metal oxide semiconductor thin-film transistors (TFTs). These TFTs have high carrier mobility, low leakage current and a wider bandgap compared with silicon. Etching the channel material to a precise and controlled thickness is important for device performance. Thermal atomic layer etching (ALE) of these metal oxide semiconductors is possible using surface modification and volatile release reactions.

In this study, the thermal ALE was performed with sequential exposures of boron trichloride (BCl3) and hydrogen fluoride (HF). In situ spectroscopic ellipsometry (SE) measurements on flat films determined etch rates for IGO of 2.1 Å/cycle at 225°C and 3.0 Å/cycle at 255°C. The etch rate for IGZO was 2.5 Å/cycle at 205°C and 5.6 Å/cycle at 255°C. The etch rates were observed to be nearly self-limiting versus the BCl3 and HF exposures.

Quadrupole mass spectrometry (QMS) investigations identified the volatile products during the BCl3 and HF exposures on In2O3, Ga2O3 and ZnO powders. The initial BCl3 exposure reacted with the In2O3, Ga2O3 and ZnO powders and produced InCl3, GaCl3 and ZnCl2, respectively. These products are consistent with conversion to B2O3. The next HF exposure then produced BF3 and H2O from the spontaneous etching of B2O3. The HF then proceeded to yield additional H2O from the fluorination of the metal oxide. The subsequent BCl3 exposure first yielded BF3 from ligand-exchange with the metal fluoride. The BCl3 exposure then proceeded to produce metal chloride by conversion of the underlying metal oxide. The QMS results for Ga2O3 powder are displayed in **Figure 1**.

Additional studies on flat films explored the effect of IGO composition on the etch rate. **Figure 2** shows that the IGO etch rates were 2.8, 3.6, and 4.2 Å/cycle at In:Ga ratios of 1:1, 2:1 and 4:1, respectively at 230 °C. The etch rate then decreased to 0.8 Å/cycle at an In:Ga ratio of 8:1. The thermal ALE was also observed to smooth the initial roughness of the IGZO surface.

11:00am **AP+EL+PS+TF-WeM-13 Isotropic Atomic Layer Etching via Thermal-Cyclic Processing: Broad Material Capabilities with a Focus on Work–Function Metal Films**, ***Kazunori Shinoda,*** Hitachi High-Tech Corporation, Japan*; Thi-Thuy-Nga Nguyen, Shunya Hirai,* Nagoya University, Japan*; Nobuya Miyoshi,* Hitachi, Ltd., Japan*; Masaru Izawa,* Hitachi High-Tech Corporation, Japan*; Kenji Ishikawa, Masaru Hori,* Nagoya University, Japan **INVITED**

An isotropic atomic layer etching (ALE) process based on thermal–cyclic processing (thermal-cyclic ALE), consisting of repeated plasma exposure and infrared lamp heating, has been developed for advanced semiconductor manufacturing applications. This approach enables highly controllable and selective isotropic material removal through self–limiting surface reactions driven by cyclic thermal activation. A key advantage of this approach is the independent optimization of the adsorption and desorption temperatures, which enables enhanced material selectivity, improved surface smoothness, and sufficient etch per cycle (EPC). To realize this process at a manufacturing scale, a dedicated 300–mm wafer tool, referred to as a Dry Chemical Removal (DCR), has been developed and commercialized. Using this DCR tool, isotropic ALE processes have been developed for a wide range of materials used in semiconductor device fabrication, including oxides, nitrides, carbides, metals, and compound films. Furthermore, surface reaction mechanisms during the ALE steps have been systematically investigated using in–situ X–ray photoelectron spectroscopy (XPS), providing direct insight into adsorption and desorption steps governing the self–limiting etching behavior. These analyses reveal material–dependent reaction pathways and clarify the roles of plasma–induced surface modification and thermally activated removal of the modified surfaces. This invited presentation provides a comprehensive overview of the thermal–cyclic ALE technology, covering its historical development, process fundamentals, tool design, and mechanistic understanding across multiple material systems.In particular, recent progress in the isotropic ALE of work–function metal films, such as TiC and TiN, will be highlighted, with an emphasis on surface reaction mechanisms investigated by in–situ XPS. These materials are of increasing importance for advanced semiconductor devices, where precise thickness and surface control are critical. Process characteristics and surface chemistry insights obtained by in–situ XPS will be discussed.

11:30am **AP+EL+PS+TF-WeM-15 Selective Thermal Chemical Vapor Etching (CVE) and Atomic Layer Etching (ALE) of Ge Versus Si**, ***Micah Duffield,*** *Marcel Junige, Steven George,* University of Colorado at Boulder

The fabrication of gate-all-around nanosheet transistors employs multi-layer stacks of crystalline SiGe and Si. Completely removing sacrificial SiGe and precisely recessing SiGe may be accomplished by chemical vapor etching (CVE) and atomic layer etching (ALE), respectively. Facile Si CVE has been shown previously using anhydrous HF vapor above 150°C. This Si CVE is ceased by co-dosing H_2O+HF. The present work explored selective CVE and ALE pathways for Ge compared with Si using HF only or with oxidants.

Quadrupole mass spectrometry (QMS) measurements identified the volatile etch products during different reactant gas exposures at ramped or isothermal temperatures. Exposing Ge nanopowder to HF during an up-ramp from 25 to 400°C discovered that facile Ge CVE produced volatile GeF_4 at 50-75°C and then turned off due to non-volatile GeF_2 polymer formation. The GeF_2 polymer could then be volatilized at >300°C. Additional experiments at varied ramp rates, a reversed down-ramp, and isothermal HF exposures corroborated this non-volatile GeF_2 polymer formation.

Exposing a mixture of Ge & Si nanopowders to HF during a temperature ramp showed that the GeF_4 etch product in turn etched Si, producing volatile SiF_4 at 75-110°C (**Figure 1a**). Co-dosing H_2O+HF still etched Ge (or GeO_2) and produced volatile GeF_4. However, co-dosing H_2O+HF eliminated

the parasitic Si etch pathway via GeF_4 (**Figure 1b**). Introduced H_2O oxidized Si and formed an ultra-thin chemical oxide. This SiO_2 was not etched by GeF_4.

Repeatedly exposing GeO_2 nanopowder to HF at 100°C revealed that GeO_2 etched spontaneously without the self-termination observed for Ge. This finding inspired a unique Ge ALE mechanism: A first oxidant exposure may oxidize Ge to form an ultra-thin GeO_2 surface layer. A subsequent HF exposure may volatilize this GeO_2 surface layer but self-terminate on the underlying Ge due to GeF_2 polymer buildup. The following oxidant exposure may remove the GeF_2 polymer and again oxidize Ge.

Exposing Ge nanopowder to a sequence of oxidant and HF exposures at 100 and 150°C, respectively, revealed that volatile GeF_4 was released after each oxidant exposure in a self-terminating fashion. To refresh the Ge surface after HF exposures, H_2O was ineffective, whereas O_2 was effective, and O_3 was even more effective than O_2 (**Figure 2**). To verify these QMS findings, *in situ* spectroscopic ellipsometry (iSE) studies were employed on Ge thin film samples. Ge ALE using an alternating O_2/HF sequence at 150°C exhibited an etch per cycle of 1.38 Å, near-ideal ALE synergy of 97%, and selectivity versus Si (**Figure 3**).

11:45am **AP+EL+PS+TF-WeM-16 Controlled SiO_2 Etch Rates Using a HF/H_2O Liquid-Layer in a Vacuum Environment: Dependence on H_2O and HF Pressures**, ***Samantha Rau,*** University of Colorado at Boulder*; Antonio Rotondaro, Hanna Paddubrouskaya, Kate Abel,* Tokyo Electron America, Inc.*; Steven George,* University of Colorado at Boulder

Our earlier research demonstrated SiO_2 etching by HF using a H_2O liquid-layer in a vacuum environment. The current work characterized the dependence of SiO_2 etch rate on the H_2O and HF pressures. We have observed a dramatic increase in SiO_2 etch rates at higher H_2O and HF pressures. This behavior suggests that the thickness of the HF/H_2O liquid-layer may be increasing rapidly at higher pressures.

SiO_2 etch rates may be sensitive to the HF/H_2O liquid-layer thickness when the thickness is close to the size the hydrated F^-, HF_2^- and SiF_6^{2-} ions that are involved during SiO_2 etching. For example, the size of the hydrated F^- ion is 7 Å. Lower SiO_2 etch rates may result from incomplete hydration of these ions. SiO_2 etch rates may approach the SiO_2 etch rates observed in solution for thicker liquid-layers.

Investigations were performed to determine the thresholds for HF/H_2O condensation versus H_2O and HF pressure. Spectroscopic ellipsometry was employed to measure the liquid-layer thickness, the mean squared error (MSE) in the thickness model, and the transmitted light intensity. Condensation was assumed to occur when the increase in liquid-layer thickness, the increase in MSE, and the decrease in light intensity all occurred rapidly at higher H_2O and HF pressures. Figure 1 shows that rapid changes in the liquid-layer thickness, MSE and transmitted light intensity are observed at a total pressure of 22.9 Torr (18 Torr H_2O and 4.9 Torr HF) at 30.4°C.

Experiments were conducted at initial H_2O pressures from 0-35 Torr and increasing HF pressures from 0-40 Torr to determine the threshold H_2O and HF pressures for condensation at 30.4°C. The resulting condensation points were then compared with the measured SiO_2 etch rates at various H_2O and HF pressures in Figure 2. Below the condensation curve in the ultrathin liquid layers, there were lower SiO_2 etch rates ranging from ~1-100 Å per 5 s HF exposure. These lower SiO_2 etch rates may result from incomplete hydration of the F^-, HF_2^- and SiF_6^{2-} ions. Above the condensation line, the measured SiO_2 etch rates of ~100-1000 Å per 5 s HF exposure were comparable with SiO_2 etch rates in bulk HF solutions with HF wt% values of 25-40%.

12:00pm **AP+EL+PS+TF-WeM-17 Thermal Selective Etching of $Si_{1-x}Ge_x$ in XeF_2**, ***Daniel Cho,*** *Yi Chen,* UCLA*; John Hoang, Nick Altieri, Ji Zhu, Samantha Tan,* Lam Research Corporation*; Jane P. Chang,* UCLA

In GAAFET fabrication, $Si_{1-x}Ge_x$ is etched selectively from Si. Wet, plasma, and thermal chemistries have been investigated to etch $Si_{1-x}Ge_x$ with a range of selectivity [1]. Thermal fluorine-based etch processes, including F_2 and XeF_2, show high selectivity with etch rates exhibiting a volcano-shaped dependence on x [2, 3].

In this study, we report $Si_{1-x}Ge_x$ (x = 0 to 1) etch by a XeF_2 beam. XeF_2 was sublimed into an expansion chamber to a target pressure, then pulsed into the reaction chamber. In each pulse, ΔP_{XeF2} was proportional to the XeF_2 dose. *Ex situ* x-ray photoelectron spectroscopy (XPS) identified the chemical bonding states on the $Si_{1-x}Ge_x$ surface from XeF_2, while scanning electron microscopy (SEM) measured the etch depth for etch rate (ER) calculations.

XeF_2 exposure on as-received $Si_{1-x}Ge_x$ samples showed no etch, confirmed by XPS and SEM. This was attributed to a native oxide which prevented XeF_2 from interacting with the underlying $Si_{1-x}Ge_x$. Prior to XeF_2 exposure, *in situ* Ar ion sputtering was used to remove the native oxide for all sequential etch conditions.

XPS results of XeF_2-processed $Si_{0.75}Ge_{0.25}$, Si, and Ge identified Ge-F, Si-F, and C-F bonding in the F 1s region at binding energies of 685.0 eV, 687.1 eV, and 689.6 eV, respectively, consistent with literature values [4-6]. Ge-F, Si-F, and C-F made up 20.8%, 37.4%, and 41.8% of the total fluorine content on the XeF_2-processed $Si_{0.75}Ge_{0.25}$. Quantitative analysis of fluorination by *ex situ* XPS was limited by air exposure between etch and measurement.

Synergistic etching, with Ar ions and XeF_2 simultaneously exposed, showed a Si ER of 6 nm/pulse at an ion beam voltage of 200 V and ΔP_{XeF2} =0.5 Torr, showing a higher ER than the sequential Si ER of 0.4 nm/pulse at the same ion beam voltage and ΔP_{XeF2}.

The peak sequential $Si_{1-x}Ge_x$ ERs for the following Ar ion beam voltage and ΔP_{XeF2} conditions, 100 V and 0.5 Torr, 200 V and 0.5 Torr, and 100 V and 0.2 Torr, were 7.8 nm/pulse, 9.9 nm/pulse, and 4.1 nm/pulse, respectively. For all conditions, ER increased from x = 0 to 0.1, followed by a decrease or plateau past x = 0.15. Higher pretreatment ion beam voltage and higher ΔP_{XeF2} both led to an etch rate increase for x = 0 to 0.25. The peak $Si_{1-x}Ge_x$/Si etch selectivity ranged from 20 to 30 under all conditions.

This research was supported by Lam Research Corporation. The development of the experimental system was partially supported by the U.S. DOE, Office of Science, as part of the ELMIC MSRC through the Plasma-enabled 2D Materials project at PPPL, under contract No. DEAC02-09CH11466.

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Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+2D+EL+EM+PS+TF-WeA

Atomic Scale Processing to Enable 2D Materials

Moderators: Dr. Robert Bruce, IBM Research, T. J. Watson Research Center, **Prof. Dr. Cristina Satriano**, University of Catania

2:15pm **AP+2D+EL+EM+PS+TF-WeA-1 Chemistry (and Some Physics) of Atomic Layer Deposition of Two-Dimensional Metal Dichalcogenides***, **Miika Mattinen,*** University of Helsinki, Finland **INVITED**

Two-dimensional (2D) materials are of interest for a range of applications from microelectronics to sensing to energy storage and production. One of the most prominent group of 2D materials are metal dichalcogenides, some of which are semiconductors, such as the prototypical MoS_2, while others are (semi)metals such as TiS_2 and TaS_2.[1] Deposition of 2D materials with desired properties on large, often temperature-sensitive, and complexly shaped substrates is a key challenge for practical applications. Atomic layer deposition (ALD) can fulfill these requirements, but unlocking the full potential of ALD requires understanding of precursor chemistry, nucleation, substrates, and film characteristics, among other factors.[1,2]

I will discuss chemistries for deposition of a range of 2D metal dichalcogenides including MoS_2,[3] SnS_2,[4] ReS_2,[5] WS_2,[6] HfS_2 and ZrS_2[7] using thermal ALD. I will cover precursor challenges related to reactivity, thermal stability, and etching reactions. Controlling crystallinity and morphology and continuity at low thicknesses are also key challenges encountered in ALD of 2D materials. To this end, I highlight the role of substrate choice and the use of a two-step SnS_2 process where the deposited amorphous film is crystallized with mild-post deposition annealing.[4,8,9]

Plasma-enhanced ALD (PEALD) can help overcome some of the challenges encountered in thermal ALD, such as limited reactivity of many precursors. For example, few thermal chemistries are available for direct deposition on low-cost plastic substrates for flexible applications (T ≤ 150 °C). To this end, I will discuss PEALD of TMDCs including MoS_2, TiS_2, and WS_2 at record-low temperatures down to 100 °C by controlling plasma chemistry[10] I will also describe advanced ABC type processes with two plasma steps, where both the plasma chemistry (reactive radicals) and physics (low-energy ions) are used to control film growth and properties.[11]

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2:45pm **AP+2D+EL+EM+PS+TF-WeA-3 First-Principles Survey of Molybdenum ALD Precursors for MoS_2 Thin Films***, **Ian Kerby,*** *Ashlee Riedinger, Lan Li,* Boise State University

Transition metal dichalcogenides, such as molybdenum disulfide (MoS_2), are promising candidates for various semiconductor applications. A crucial requirement for these applications is the controlled and conformal deposition of a monolayer film. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) techniques are key to achieving thin films at commercial scale. Towards this end, the reactions of a variety of precursor chemicals with another variety of surfaces need to be understood. A reaction between a surface and a precursor can be difficult to study in-situ and ex-situ, making computational modeling a valuable tool for addressing this challenge. The work presented here is a survey of common and proposed molybdenum precursors for use in atomic layer deposition of MoS_2 films. Our work in modeling nucleation of these precursors includes various surfaces with the primary aim of determining the role of surface morphology and chemistry during deposition. We have conducted thermodynamic surveys using density functional theory (DFT) for spontaneity of proposed reaction pathways for the precursors to interact and nucleate on the surfaces. To generate and account for the inherent variability in the amorphous substrate, we have utilized ab-initio molecular dynamics (AIMD), enabling a more comprehensive exploration of the complex energy landscape. We have also investigated the formation of reaction residues on surfaces. Our studies lay the groundwork for future kinetic analyses. The stable intermediate states identified along the reaction pathways can be used in nudged elastic band (NEB) calculations to determine the associated energy barriers during nucleation. These insights may further help guide and inform experimental efforts.

3:00pm **AP+2D+EL+EM+PS+TF-WeA-4 Thermal and Plasma-Enhanced ALD of MoS_2 using $MoO_2(THD)_2$***, **Ryan Weiland,*** University of Michigan, Ann Arbor*; Ian Campbell,* IMEC*; Pierre Morin, Benjamin Groven,* IMEC Belgium*; Ageeth Bol,* University of Michigan, Ann Arbor

Field effect transistors (FETs) are foundational components of modern electronics. For these applications, scalability is as important as device performance. Two-dimensional MoS_2 exhibits a direct band gap and enables high fidelity electrostatic control due to its reduced dimensionality and the absence of dangling-bonds at the surface. MoS_2 is therefore an ideal channel material for future FETs. Atomic layer deposition (ALD) is a promising technique for scalable, conformal, and back-end-of-line compatible MoS_2 deposition. While promising, the electrical performance of ALD grown 2D MoS_2 does not meet expectations when compared to the electrical properties of mechanically exfoliated MoS_2, due its polycrystalline nature. Polycrystalline MoS_2 contains grain boundaries that act as scattering centers, trap-rich regions, and structural discontinuities, that degrade its desirable electronic properties. In this work, ALD processes were developed using a novel molybdenum precursor, $MoO_2(THD)_2$. $MoO_2(THD)_2$ contains bulky organic ligands, which could impose steric hindrance during surface reactions, thus limiting surface chemisorption density and favoring formation of larger crystal grains.

First, $MoO_2(THD)_2$ volatility and decomposition behavior were studied by thermogravimetric analysis (TGA). TGA showed sublimation beginning at 120°C with 100% mass loss at 300°C. Next, plasma and thermal ALD processes were developed at 400°C. A mixed H_2S/Ar co-reactant was used for both plasma and thermal ALD. The effects of precursor and co-reactant dosing times, co-reactant ratios, as well as purge conditions were systematically investigated using in situ ellipsometry. The growth per ALD cycle (GPC) was measured to be 0.07 Å/cycle for the thermal recipe and 0.15 Å/cycle for the plasma process. The resulting films were characterized by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and atomic force microscopy (AFM). XPS indicates near-stoichiometric MoS_2. Raman spectra confirm MoS_2 vibrational modes and film crystallinity for both processes, while AFM reveals smooth, continuous films without out-of-plane features, with an RMS roughness of ~0.5 nm.

Overall, this work establishes $MoO_2(THD)_2$ -enabled thermal and plasma-enhanced ALD at 400 °C as a scalable route to smooth, continuous, and crystalline MoS_2 thin films. These results lay the groundwork for integrating conformal, large-grain MoS_2 channels into back-end-of-line compatible process flows, with ongoing grain-size quantification and electrical testing expected to link microstructural improvements to device performance.

3:15pm **AP+2D+EL+EM+PS+TF-WeA-5 Low Temperature Magnetized Plasmas for Processing of Two-Dimensional Materials***, **Yevgeny Raitses,*** Princeton Plasma Physics Laboratory*; Stanislav Musikhin, Yerbolat Ussenov,* Princeton University Plasma Physics Lab*; Satya Butler, Saien Xie,* Princeton University*; Nirbhav Chopra,* Princeton University Plasma Physics Lab **INVITED**

Low-temperature magnetized plasmas generated by electron beams or non-thermal electrons offer new opportunities for atomic-scale materials processing relevant to microelectronics and quantum technologies.[1-3] Operating at low pressures (0.1–10 mTorr), the applied magnetic field enables spatial separation between a high-density plasma generation region (~10^{11}–10^{12} cm^{-3}, electron energies >10 eV) and a peripheral processing region characterized by lower plasma density (<10^9 cm^{-3}) and electron temperatures (<1 eV).[4] Substrates placed in this region are primarily exposed to low-energy ion fluxes (≲ a few eV), enabling damageless processing of two-dimensional materials or processing with a controllable defect formation of such materials. However, plasma instabilities can drive anomalous cross-field transport and increase ion fluxes and energies at the surface.[5] We present experimental results on instability mitigation in ExB plasma systems[4] and demonstrate improved low-damage processing of graphene and transition metal dichalcogenides. Quantitative defect characterization in plasma-treated monolayered WS_2 films is presented and benchmarked against conventional RF inductively coupled plasma processing. A focus will also be made on the effect of vacuum conditions in the plasma reactor chamber on the defect formation

(e.g. sulfur vacancies). Applications to hydrogen and nitrogen surface passivation of diamond for quantum devices are also discussed.[2]

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Acknowledgement

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4:15pm **AP+2D+EL+EM+PS+TF-WeA-9 Impact of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of Crystalline MoS_2***, **Spencer Smith**, Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has emerged as a transformative technique for atomic-scale processing of two-dimensional (2D) materials, including molybdenum disulfide (MoS_2), a promising semiconductor due to its high carrier mobility in monolayer form. Precise etching of MoS_2 films offers a pathway for tuning electrical and optical properties through controlled thickness. Previous studies have explored alternative fluorination and oxygenation chemistries for thermal ALE of amorphous MoS_2, including oxygen sources such as H_2O and O_3 and fluorine sources including HF/pyridine and MoF_6. In this work, we investigate the application of these alternative chemistries to the thermal ALE of MOCVD-grown and ALD-grown MoS_2 films. Preliminary work on ALE of crystalline MoS_2 indicates that etching occurs at defects and grain boundaries. This study aims to correlate etching behavior with changes in surface topography and defect density. Etching effectiveness will be characterized by atomic force microscopy, Raman spectroscopy, and photoluminescence spectroscopy. This study seeks to further expand the capabilities of ALE for precise processing of 2D materials relevant to next-generation semiconductor devices.

4:30pm **AP+2D+EL+EM+PS+TF-WeA-10 Atomic Layer Etching of Tungsten Disulfide in O2/Ar and BCl3/Ar Remote Plasmas***, **Jeremy J. Mettler**,* University of Houston*; Jaehong (Russell) Kwon, David. B. Graves,* Princeton University*; Vincent M. Donnelly,* University of Houston

Transition-metal dichalcogenides (TMDs) are a class of 2D materials consisting of covalently bonded sheets. Multi-layers are held together by cross-plane van der Waals forces. While these materials hold promise in future semiconductor applications, processes for manufacturing using TMDs are in the early stages of development. One challenge is obtaining uniform, monolayer growth of TMD films over large areas. Chemical vapor deposition results in the formation of multilayer islands. Etching of TMD films will also be required, if for no other reason than to thin multilayers to single layers. Atomic layer etching (ALE) is likely to be called upon for etching steps. TMDs are easily damaged by high temperature and energetic species bombardment, making thermal or plasma-assisted etching challenging. We have explored ALE of WS_2, a promising TMD 2D material. A remote plasma supplied reactive radicals. A switchable magnetic field allow low energetic ion bombardment to be turned on or off while having little effect on radical density. ALE of WS_2 was achieved in a two-step process. Vacuum-transfer x-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition and thickness of the remaining film at various stages in the process. Sulfur-terminated multilayer films of WS_2 were exposed to O atoms downstream of an Ar/O_2 inductively coupled plasma (ICP). Without ion bombardment thermal O atoms removed S from the surface and formed a tungsten oxide layer 1-2 monolayers thick, with a composition of roughly WO_4. These results agree favorably with parallel molecular dynamics simulations. In the presence of low energy ions (~15 eV) at a flux of ~3 x $10^{15}cm^{-2}$, the etching rate increased several-fold and the W-oxide stoichiometry was not changed. The Ar/O_2 plasma was followed by Ar/BCl_3 plasma to selectively etch the tungsten oxide layer relative to the underlying WS_2. This step required low energy ion bombardment to remove the WO_4 film and expose the next WS_2 layer. A detailed analysis of the film at various stages in the ALE process was carried out by using the high-resolution W(4f), S(2p), B(1s) and Cl(2p) in the film as well as the Si(2p) from the underlying substrate and O(1s) in the WS_2 film and underlying interfacial native oxide layer on Si. A complete picture of the stoichiometry of the film during ALE was obtained and will be presented.

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Fusion Energy Sciences and Basic Energy Sciences, as part of the Extreme Lithography & Materials Innovation Center (ELMIC), a Microelectronics Science Research Center (MSRC), under contract No. DEAC02-09CH11466.

4:45pm **AP+2D+EL+EM+PS+TF-WeA-11 Investigation of Layer-by-Layer Etching of MoS_2 by Atomic Oxygen and XeF_2***, **Sei-won Chung**, Daniel Cho, Jane Chang,* University of California, Los Angeles

As semiconductor devices continuously scale down, the demand for channel materials of field effect transistors (FETs) with high mobility at low dimensions has increased. 2D transition metal dichalcogenides (TMDs) have gained interest due to relatively consistent mobility at 5 nm of body thickness compared to conventional silicon channel. However, non-uniform large area synthesis has been a challenge in integration. To improve device performance, non-uniform adlayers should be removed layer-by-layer to realize a uniform and large-area TMD films.

To investigate layer-by-layer etching of MoS_2, thermochemical analysis suggests thermodynamic feasibility of using oxygen and fluorine chemistries for MoS_2 etching. Individual and synergistic effects of Ar^+, O radical (produced by a coaxial waveguide microwave source) and XeF_2 (3Torr) were studied in the molecular beam where each species can be independently controlled in flux and energy. The as-received MoS_2 has S/Mo and Si/Mo ratios of 1.6 and 1.0. Neither O nor XeF_2 spontaneously reacted with the as-received MoS_2. Ar^+ ion beam (200V, 0.5mA, 10s) was used to remove surface contamination prior to etching, resulting S/Mo and Si/Mo ratios of 0.94 and 0.18 respectively. Following in-situ Ar^+ ion beam cleaning, O radical was shown to oxidize MoS_2 decreasing S/Mo from 0.94 to 0.46, while XeF_2 removes MoS_2 increasing Si/Mo from 0.18 to 7.1. It showed surface fluorination (~3%), corresponding to formation of $MoOF_x$ and CF_x.

Finally, the sequential process consisting of Ar^+ ion bombardment, O radical introduction, and XeF_2 vapor exposure (0.5T, 10 pulses) was applied which could enable surface activation, self-limiting oxidation and removal of modified layer by forming oxyfluorides. After XeF_2, O atomic composition decreased and S atomic composition increased indicating removal of MoO_3 with surface fluorination (~3%) of MoF_x and $MoOF_x$. Increasing number of pulses to 20 increases S/Mo from 1.1 to 1.4 while reducing the MoO_3 content. This research reveals the individual and combination effects of Ar^+ ion beam, O radicals and XeF_2 on MoS_2 etching and potentially applied to investigating mechanism of layer-by-layer etching of MoS_2.

This research is supported by the U.S. DOE, Office of Science, as part of the ELMIC MSRC through the Plasma-enabled 2D Materials project at PPPL, under contract No. DEAC02-09CH11466.

5:00pm **AP+2D+EL+EM+PS+TF-WeA-12 Width Reduction and Edge Smoothing of 2D MoS_2 Nanoribbons by Lateral Thermal Atomic Layer Etching***, **Janine Wyand**,* University of Colorado at Boulder*; Tara Pena, Eric Pop,* Stanford University*; Steven George,* University of Colorado at Boulder

Atomic layer etching (ALE) of 2D MoS_2 nanoribbons is important for the fabrication of MoS_2 channel transistors. E-beam lithography and conventional dry etching processes face problems when etching MoS_2 films. These disadvantages include delamination for nanoribbon widths < 25 nm and inability to control line edge roughness. ALE methods may bypass these limitations and produce narrower width MoS_2 channels with smoother edges that may have better electrostatic control and on/off switching.

Narrowing the width of 2D MoS_2 nanoribbons requires lateral etching in the 2D plane. Our earlier work on the thermal ALE of 2D MoS_2 showed that sequential exposures of O_3 and $SOCl_2$ produced lateral etching by either “outside-in” or “inside-out” mechanisms. In this study, the “outside-in” lateral etching of 2D MoS_2 crystalline nanoribbons was utilized to reduce the widths of 2D MoS_2 nanoribbons. O_3 (ozone) was used for MoS_2 oxidation to MoO_3 and $SOCl_2$ (thionyl chloride) was used for the volatilization of MoO_3 as MoO_2Cl_2. The studies were performed using high quality 2D MoS_2 nanoribbons on silicon coupons. The MoS_2 nanoribbons were prepared from monolayer 2D MoS_2 films using e-beam lithography and dry etching.

The etching of the 2D MoS_2 nanoribbons was examined by atomic force microscopy (AFM) at 150°C. The lateral etching could be quantified by returning to the same nanoribbon after various numbers of etching cycles

and measuring the nanoribbon width using AFM. **Figure 1** shows that the width of the nanoribbons decreases progressively versus number of etching cycles. The AFM images indicate that the etching cycles also smooth the nanoribbon line edge roughness.

The AFM images were consistent with lateral etching at the edges of the 2D MoS_2 nanoribbons. The AFM measurements determined that the 2D lateral etching rate was ~3.9 Å per etching cycle at 150°C as displayed in **Figure 2**. This lateral etch rate represents ~1 MoS_2 units removed per etching cycle at the step edge of the 2D MoS_2 crystalline domains. Additional AFM measurements revealed that nanoribbon widths < 25 nm were possible using this thermal ALE process.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+MS+PS+TF-ThM

Advancing Spectroscopic Ellipsometry and Other in-Situ Techniques to Enable Atomic Scale Processing

Moderators: Prof. Dr. Marcel Junige, University of Colorado at Boulder, **Dr. Adrie Mackus**, Eindhoven University, Netherlands

8:00am **AP+EL+MS+PS+TF-ThM-1 Atomic Processes in Surface-Limited ALD Growth Studied by Real-Time Spectroscopic Ellipsometry**, ***Eva Schubert***, *Ufuk Kilic, Yousra Traouli, Mathias Schubert,* University of Nebraska - Lincoln **INVITED**

We employ in-situ spectroscopic ellipsometry (SE) to investigate the growth dynamics of ultrathin transition metal oxide films (ZnO, WO_3, TiO_2, and Ga_2O_3) during plasma-enhanced atomic layer deposition (PE-ALD). To analyze the dynamic optical response, we introduce a dual-box regression model in which the first box represents surface roughness using an effective medium approximation (EMA), while the second box captures cyclic variations in subsurface layer thickness associated with molecular rearrangements occurring during each ALD cycle. This approach provides a time-resolved and quantitative description of both surface roughness evolution and subsurface film growth dynamics, enabling accurate characterization of layer-by-layer deposition processes.

Accurate extraction of film thickness, density, and roughness at elevated substrate temperatures requires precise knowledge of the temperature-dependent dielectric function (TDF), which can differ substantially from room-temperature values. In this work, the TDFs of the transition metal oxides were determined through multi-sample analysis using optical data obtained from films of varying thicknesses measured at different stages of the growth process. The incorporation of experimentally verified dielectric functions enables the dual-box model to reliably describe the evolving optical response during high-temperature deposition, allowing detailed monitoring of sub-monolayer coverage, interface formation, and roughness evolution throughout the ALD process.

Post-deposition structural and chemical characterization using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) corroborates the in-situ optical measurements and provides complementary insight into film crystallinity, morphology, and composition.

The capability of in-situ ellipsometry as a powerful tool for investigating growth dynamics will also be demonstrated for multilayer fabrication, ultra-precise thickness control, and monitoring of phase transitions in materials synthesized using physical and chemical vapor deposition techniques.

8:30am **AP+EL+MS+PS+TF-ThM-3 Tracking Critical Points: In Situ Ellipsometry for Rapid Assessment of Atomic Layer Processes on III-V Interfaces**, ***John Murphy***, *Glenn Jernigan, Michael Johnson, David Boris, Scott Walton, Jill Nolde,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer processing (PE-ALD, ALE) on semiconductor interfaces, especially III-V semiconductor interfaces, requires precise control of plasma–surface interactions to achieve oxide-free interfaces and low-defect dielectric interfaces. Conventional post-process characterization (XPS, AFM, CV profiling) is time-consuming and inefficient for navigating large, nonlinear plasma process parameter spaces. In this work, we demonstrate an *in situ* spectroscopic ellipsometry (SE) methodology that provides a real-time, model-light assessment of III-V surface quality by tracking high-energy critical-point amplitudes directly from the pseudodielectric function, without constructing full multilayer optical models. Notably, critical points in the 4–5 eV range have photon penetration depths of ≈10 nm in III-V semiconductors, making them highly sensitive to near-surface chemistry.

This methodology is illustrated on InAs (100) surfaces during remote Ar/H2 plasma treatments, aimed at reducing native oxides. In the case of InAs (100) surfaces the E_0' critical point (≈4.4 eV) is used as the primary surface-quality metric during plasma treatments. While second-derivative analysis of the directly measured pseudodielectric function provides temperature dependent energy positions for critical points and the magnitude of which are calibrated using chemically clean reference surfaces.

Variations in the normalized E_0' amplitude are monitored as function of various substrate temperatures (100–300 °C), plasma powers (100–500 W), and H_2 flow fractions (1.25–6.25%) to capture the interplay between oxide removal, metallic species formation, and plasma-induced disorder with greater sensitivity and immediacy than conventional XPS metrics. These variations can be used to rapidly define practical processing windows and enable efficient down-selection within large plasma parameter spaces. The results highlight a generally useful strategy for integrating in situ critical-point tracking into atomic layer processing of III-V materials and suggest straightforward extensions to other compound semiconductor and dielectric growth environments.

8:45am **AP+EL+MS+PS+TF-ThM-4 Intelligent Sustainable ALD Research Platform Integrating On-Demand Precursor Delivery with *in situ* Imaging Ellipsometry**, ***Takeshi Momose***, *Hiroshi Nishizato,* Kumamoto University, Japan*; Yugo Nakaya,* HORIBA STEC, Co., Ltd. / Kumamoto University, Japan*; Kanta Ishida, Shota Oda, Kinichi Nasu,* Kumamoto University, Japan*; Lianhua Jin,* University of Yamanashi, Japan*; Hiroshi Okajima,* Kumamoto University, Japan

The development of efficient and sustainable processes in atomic layer deposition (ALD) is becoming increasingly important for the fabrication of next-generation three-dimensional (3D) semiconductor devices. However, conventional run/vent precursor delivery systems are inherently inefficient, with precursor dosing durations reported to be only 1-10% of the total cycle time, resulting in over 90% of the precursor being discarded without contributing to film growth. Furthermore, the development of the ALD process, especially the conformality of high-aspect-ratio (HAR) features, typically relies on time-consuming offline characterizations. In this study, we developed an integrated intelligent ALD research platform that combines on-demand precursor delivery with *in situ* imaging ellipsometry for real-time conformality analysis.

The platform integrates two key technologies. First, to achieve stable and precise on-demand precursor delivery, we developed an in-house piezoelectric-valve system. By applying a machine learning (ML) and control engineering approach, we achieved feedforward valve control, thereby successfully compensating for the inherent hysteresis and nonlinear flow responses of the valve. This allowed the achievement of ideal step-wise gas pulses with a settling time of only 60 ms, compared with 2 s in the uncontrolled condition. This precise control significantly enhances the precursor utilization efficiency while maintaining rapid pulse operation. Second, an in-house lateral high-aspect-ratio (LHAR, AR = 300) test structure combined with imaging ellipsometry was employed to quantitatively monitor the temporal evolution of the precursor penetration depth (PD) during ALD. Sample imaging was enabled by installing an Offner optical system on our custom-built ellipsometer, which allowed us to determine the PD formed in a groove on the Si substrate. As this is currently in an offline setting, we plan to install it in an ALD chamber with on-demand precursor delivery for real-time PD monitoring.

The integration of these technologies enables the instantaneous evaluation of the effect of precise changes in the precursor dose and pulse duration on conformality within HAR features. Initial experiments using trimethylaluminum (TMA) demonstrated that PD evolution in LHAR structures could be tracked. The proposed platform concept leads to a foundation for data-driven, low-waste, and rapidly adaptive ALD process development, contributing to reduced precursor consumption, shorter development cycles, and more sustainable atomic-scale manufacturing.

9:00am **AP+EL+MS+PS+TF-ThM-5 Real-Time Insights into Plasma-Based Atomic-Scale Processing via Ellipsometry**, ***Gottlieb Oehrlein***, University of Maryland College Park **INVITED**

Single-wavelength ellipsometry (SWE) has been employed as an attractive diagnostic technique for real-time, non-invasive monitoring of thin-film evolution during semiconductor processing. Characterized by high temporal resolution and sub-angstrom sensitivity, SWE allows for the precise detection of surface modifications without disrupting the plasma environment. These aspects, combined with relative ease of integration into complex process chambers, make SWE a premier tool for tracking atomic-scale processing. Because of its rapid sampling capabilities, SWE is an invaluable tool for probing the primary kinetics of plasma-surface interactions. We will discuss several case studies where ellipsometric monitoring provides critical insights into complex surface mechanisms, including the achievement of high material etching selectivity for dielectric materials, semiconductors and metals, atomic layer etching (ALE), and the dynamics of electron-beam enhanced remote plasma processing.

While ellipsometry excels at tracking processes including endpoints across diverse materials, optical data alone cannot resolve complex surface chemistry. This talk emphasizes the methodological importance of coupling ellipsometric data with chemical analysis, e.g. X-ray Photoelectron Spectroscopy (XPS) or other materials characterization techniques, to

construct robust, chemically informative surface models. Integrating these complementary diagnostics bridges the gap between optical observations and fundamental chemical mechanisms.

Acknowledgements

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9:30am **AP+EL+MS+PS+TF-ThM-7 Spectroscopic Ellipsometry for Screening Chemical and Microstructural Properties of MoS_2 Thin Films Grown by Plasma Enhanced ALD***, **Douglas Heine,*** University of Michigan, Ann Arbor*; Paula Arellano,* University of Michigan*; Ageeth Bol,* University of Michigan, Ann Arbor

The two-dimensional layered semiconductor MoS_2 has attracted significant interest for applications in next-generation electronics, photonics and electrocatalysis due to its favorable electronic and optical properties. Plasma-enhanced atomic layer deposition (PEALD) provides a scalable route for the growth of MoS_2 thin films, offering excellent thickness control, conformality, and relatively low deposition temperatures, which are advantageous for integration into device architectures. However, PEALD grown MoS_2 films often exhibit complex microstructures, consisting of small and misaligned grains. Such structural disorder can adversely affect device performance due to the strong optical and electronic anisotropy of MoS_2[(1)].

In this presentation, we report the development of a model that rapidly estimates electronic and microstructural properties of PEALD-grown MoS_2 thin films from ellipsometry data. The influence of misaligned, out-of-plane oriented grains (“fins”) is described using a Bruggeman effective medium approach for intrinsically anisotropic inclusions[(2)], while local structural disorder is incorporated through modest variations in the intrinsic optical constants. The model is applied to a broad set of films grown under different deposition conditions, and the extracted parameters are correlated with independently measured film properties, including composition, crystallinity and roughness. By enabling rapid insight into the film microstructure and electronic properties, this ellipsometry-based analysis facilitates the development of PEALD processes that yield higher quality MoS_2 films.

(1) Toolbox of Advanced Atomic Layer Deposition Processes for Tailoring Large-Area MoS2 Thin Films at 150 °C. M. Mattinen et al. ACS Applied Materials & Interfaces, 2023 15 (29), 35565-35579.

(2) Bruggeman formalism versus “Bruggeman formalism”: particulate composite materials comprising oriented ellipsoidal particles. T. G. Mackay and A. Lakhtakia. Journal of Nanophotonics, 2012 6 (1), 069501-069501.

9:45am **AP+EL+MS+PS+TF-ThM-8 Monitoring Electron Beam-Assisted Atomic Layer Etching via Real-Time Ellipsometry and in-Situ XPS: Insights on the Early Stages***, **Vennela Vuruputuri,*** Department of Physics, and Institute for Research in Electronics and Applied Physics, University of Maryland*; Robert Bruce,* IBM TJ Watson Research Center*; Nathan Marchack,* IBM TJ Watson Center*; Marinus Hopstaken,* IBM TJ Watson Research Center*; Gottlieb Oehrlein,* Department of Material Science and Engineering, and Institute for Research in Electronics and Applied Physics, University of Maryland

Electron beam assisted etching of plasma functionalized materials has emerged as a novel approach to processing damage sensitive materials. This method employs synergistic interactions between low energy electrons and reactive neutral species to enable material removal while mitigating ion bombardment induced damage and achieving higher atomic precision. While this seems to be a promising approach, the influence of electron irradiation on surface chemistry, defect formation and bond scission are not well understood. Clarifying these mechanisms is essential to establishing electron beam-assisted atomic layer etching (EB-ALE) as a viable method for nanoscale fabrication. In this work, we investigate the EB-ALE of chlorinated single crystal silicon (c-Si) surfaces prepared using a remote plasma source with Ar/Cl_2 gas mixtures. The study examines the dependence of surface coverage, material modification and etching behavior on key parameters, including neutral exposure, and flood gun parameters like electron energy and dose delivery. ALE relies on self-limiting surface reactions, and one key question is if the EB-ALE process can maintain a constant etch depth per cycle as surface roughness, defect or byproduct accumulation evolve. The surface evolution is monitored in real time using in-situ ellipsometry, and it is further characterized using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to analyze changes in chemical composition and surface roughness respectively. Together, these measurements will provide a framework to better understand the mechanisms governing EB-ALE and ensure predictive control over low-damage atomic scale processing.

Acknowledgements

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11:00am **AP+EL+MS+PS+TF-ThM-13 Building Intelligence Through in Situ Techniques for Atomic Layer Processes***, **Parag Banerjee,*** University of Central Florida **INVITED**

Note: This abstract was initially for TF, but I request that the talk be moved to Gary W Rubloff (GWR) Symposium as it is much more topically relevant.

Atomic layer processing, which consists of atomic layer deposition (ALD) and atomic layer etching (ALE), provides the ultimate processing toolbox for dimensional and compositional control of thin films. In this talk, I will first provide a historical perspective of how specifically, *in situ* techniques implemented for atomic layer processes have impacted our understanding of surface physical and chemical mechanisms that impart atomic layer processes their singular deposition and/or etching characteristics. For example, early work using *in situ* techniques such as, quadrupole mass spectrometry (QMS), Fourier transform infrared spectroscopy (FTIR) and quartz crystal microbalance (QCM) laid the foundation for understanding of the popular ALD chemistries of Al_2O_3 and ZnO. Next, I will showcase the use of *in situ* QMS and spectroscopic ellipsometry (SE) to rapidly screen new precursor molecules and deposit materials for a myriad of applications ranging from lasing fibers to passivation contacts for solar cells. The use of tandem *in situ* techniques will be highlighted which allows for unambiguous determination of both chemical and physical aspects of growth mechanisms during atomic layer processes. Last, due to the massive amounts of data obtained during *in situ* monitoring of processes, machine learning (ML) algorithms can now be successfully used to interpret process performance against process parameters, determining end points and establishing process – property causality. In summary, this presentation highlights the evolution of atomic layer diagnostics from foundational surface chemistry to modern, AI-driven process optimization.

11:30am **AP+EL+MS+PS+TF-ThM-15 Real Time Spectroscopic Ellipsometry and Passivation Studies of Ultra-Thin a-Si:H Films for C-Si / a-Si:H Heterojunction Solar Cells***, **Venkanna Kanneboina,*** *Prabin Dulal, Bishal Bishal Shrestha, Madan K. Mainali, Balaji Ramanujam, Ambalanath Shan, Nikolas J. Podraza,* University of Toledo

High passivation quality and excellent electronic properties of ultrathin hydrogenated amorphous silicon (a-Si:H) layers are essential to fabricate high efficiency crystalline silicon (c-Si) / a-Si:H heterojunction intrinsic thin layer (HIT) solar cells. The quality of the surface passivation of both undoped and doped a-Si:H layers deposited on c-Si are studied using minority carrier lifetime (τ_{eff}) measurements. Stacks of undoped a-Si:H / n-type c-Si / undoped a-Si:H, n-type a-Si:H / undoped a-Si:H / n-type c-Si / undoped a-Si:H / n-type a-Si:H, n-type a-Si:H / undoped a-Si:H / n-type c-Si / undoped a-Si:H / p-type a-Si:H are fabricated by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD). Real time spectroscopic ellipsometry (RTSE) is performed to monitor growth during the deposition of the stacks to determine the structural and optical properties of the undoped and n- and p-type doped a-Si:H. To prevent epitaxial growth on the c-Si wafers, the first layer of undoped a-Si:H is deposited at relatively low temperature of 120ºC without hydrogen dilution followed by a second layer of higher quality undoped a-Si:H with hydrogen dilution deposited at 160ºC. The influence of additional hydrogen plasma treatment (HPT) on the passivation quality of a-Si:H layers on c-Si is studied by subjecting the undoped a-Si:H on both sides of the c-Si wafers to a hydrogen plasma. Passivation studies are performed on stacks of undoped a-Si:H deposited on both sides of c-Si, and then with an additional stack of doped a-Si:H. The symmetrically deposited bilayers of undoped a-Si:H effectively passivated the c-Si. The best τ_{eff} = 11.61 ms is obtained with HPT on undoped a-Si:H bilayers for 30 seconds at 200ºC. The sample is exposed to atmosphere for about 30 min before it is loading into PECVD chamber and the measured τ_{eff} is 8.25 ms prior to deposition of the n-type a-Si:H. The τ_{eff} is recovered about 3 ms with doped n-type a-Si:H stack, whereas 1 ms is recovered with the n- and p-type a-Si:H stack. The passivation quality of single layer of ~6 nm undoped a-Si:H is also studied with variation of temperature from 120 – 200ºC. In this case, the τ_{eff} decreased from 3.85 to 1.6 ms as the temperature increased from 120 – 200ºC. High efficiency c-Si / a-Si:H HIT solar cells are fabricated using these optimized, high quality ultrathin a-Si:H layers.

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11:45am **AP+EL+MS+PS+TF-ThM-16 Quantifying Interface Formation in InP/Al_2O_3: ALD Films Probed by XPS and MIS C-V**, ***Fabiano Borges,*** University of Campinas (Unicamp) and Federal Institute of Education, Science and Technology of São Paulo (IFSP), Brazil*; Cassio Almeida,* Semiconductor Laboratory (LabSem), Center for Telecommunication Studies (CETUC), Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Brazil*; Ângela Albuquerque,* Brazilian Nanotechnology National Laboratory (LNNano, Brazilian Center for Research in Energy and Materials (CNPEM)), Brazil*; Gustavo Vieira,* Institute for Advanced Studies (IEAv), Department of Aerospace Science and Technology (DCTA), Brazilian Air Force, Brazil*; José Diniz,* University of Campinas (UNICAMP), Brazil

Abstract

Surface passivation of n-type InP was evaluated by X-ray Photoelectron Spectroscopy (XPS) depth-profile analysis after depositing an Al_2O_3 layer [1] with and without plasma treatments (oxidation (O2), nitriding (N2), oxidation followed by nitriding (O2N2), and nitriding followed by oxidation (N2O2)). To compare samples, we use the atomic fractions of Al2p, In3d, P2p, O1s, N1s, and C1s and two metrics [2]: top-film O/Al ratio at the first depth, with values near 1.5 indicating stoichiometric Al_2O_3*;* (ii) interface depth, the etch time where the sum of In+P≥20%.

The data show that O2 yields a stoichiometric surface (O/Al = 1.37) and the deepest interface (75s), consistent with a thicker interfacial oxide. N2 presents a very low O/Al (0.12) with detectable N and no interface onset within 120s, indicating a dense nitride/oxynitride barrier. N2O2 is intermediate (O/Al=1.42; interface 50s) with no residual N, suggesting oxidation of the nitride. The control sample shows oxidation (O/Al=0.51; interface 45s), while O2+sputtering produces the lowest O/Al (0.14) and the shallowest interface (35s), indicative of a less oxidized/less dense film.

Electrical C-V corroborates the chemical trends: the O2 sample exhibits a median flat-band voltage Vfb=0.00V (-0.30V for the control) and a donor density of the same order (2×10^{19} vs 1×10^{19} cm^{-3}), indicating a flatter band alignment without doping degradation. Altogether, O2 delivers the most stoichiometric Al_2O_3*,* a thicker/interfacial oxide and superior C-V metrics, pointing to improved passivation of InP compared with ALD on untreated surfaces; N2 forms a robust nitride that retards sputter breakthrough; and ALD delivers denser, more stoichiometric Al_2O_3 than sputtering.

References

[1] X. Liu et all, “Interface optimization and performance enhancement of InP MOS capacitors with Sm_2O_3/Al_2O_3 gate stacks,” *Semicond. Sci. Technol.*, vol. 36, n. 10, p. 105013, 2021.

[2] A. G. Shard, “A step-by-step guide to X-ray photoelectron spectroscopy (XPS),” *J. Appl. Phys.*, vol. 131, no. 6, p. 061101, 2022.

Acknowledgments

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Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+MS+PS+TF-ThA

Advancing Atomic Scale Processing Through Novel Sources and Pulsing Methods

Moderators: Dr. Keren Kanarik, Lam Research Corporation, **Prof. Dr. Han-Bo-Ram Lee**, Incheon National University

2:15pm **AP+EL+MS+PS+TF-ThA-1 High-Throughput Silicon ALE via Rapid Matchless Power Modulation**, ***Banks Peete,*** North Carolina State University*; Jeremy Mettler,* University of Houston*; Paul Melnik,* EHT Semi*; Shreeyansh Rastogi, Zuhair Khan,* University of Houston*; Chris Bowman, James Prager, Timothy Ziemba,* EHT Semi*; Steven Shannon,* North Carolina State University*; Vincent Donnelly,* University of Houston

By leveraging rapid, multi-level power modulation, we have expanded the self-limiting window of continuous gas flow atomic layer etching (ALE) of silicon to higher chlorine flow rates enabling much quicker ALE cycle periods. ALE offers superb controllability, but it is limited in speed by the time it takes to purge and switch gases from the chamber. Previously, a continuous flow of argon and chlorine gases were injected into continuously-powered, inductively-coupled plasma (ICP) while the bias power to the substrate stage was pulsed on for 0.2 s and off for 1 s. When the chlorine flow was kept in a narrow window, the silicon chloride surface layer was removed by argon ions faster than the surface can re-chlorinate. At higher chlorine flow rates, this process collapsed into traditional reactive ion etching.

In this work, we expand this “ALE window” by modulating the ICP power in sync with the bias-on period. This was accomplished using a matchless power generator (EHT Semi “Orion”), capable of rapidly changing power levels by an order of magnitude in microseconds. The matchless capabilities ensure that power is still delivered efficiently during the large change in plasma impedance. Time-resolved hairpin probe measurements confirm electron density transition times between power states in the hundreds of microseconds time-scale, far faster than would be possible with a traditional matching network based power delivery system. By operating the ICP at 300W during the bias-off period and at higher powers (600 W to 1.5 kW) during the bias-on period, the ALE window can be expanded to higher chlorine flow rates. During the bias off phase, the higher chlorine flow rates re-chlorinate the surface faster, decreasing the total ALE cycle time. Time-resolved optical emission spectroscopy of the SiCl (280.75 nm) line was used as a real-time monitor of the relative etching rates. At higher chlorine flows, the line exhibited a “spike and decay” profile indicative of ALE, unlike the previous work with constant 300 W power, which showed a square wave-like response to the bias turning on that is associated with simple pulsed reactive ion etching. This confirms that syncing the bias with a higher level ICP power enables higher chlorine flow rates while still outrunning re-chlorination.

2:30pm **AP+EL+MS+PS+TF-ThA-2 Etching Commercially-Relevant Materials Using Tailored Waveform Biasing**, ***Benjamin Harris,*** *Daryl White, Kate Stokes, Matthew Loveday, James Ellis, Geoffrey Hassall,* Oxford Instruments Plasma Technology, UK

Control of the ion energy distribution function (IEDF) in a plasma is essential for optimising etch processes, such as atomic layer etching (ALE) and reactive ion etching (RIE). If the ion energy is too low, ions will fail to etch the surface of a material. If the ion energy is too high, ions may induce subsurface damage by sputtering material below the surface layer. Between these two boundaries lies the optimal range for ion energies, where ion utilisation is maximised and subsurface damage is minimised. Historically, a radio-frequency, sinusoidal bias is applied to the wafer table to control the IEDF near the wafer surface. This produces bimodal IEDFs with characteristic widths on the order of tens of eV, which is often wider than the optimal window for etching industrially-relevant materials [1]. Tailored waveform biasing (TWB) provides an alternative to radio-frequency biasing that offers enhanced control over the width and mean energy of the IEDF.

In this study, TWB is used to sputter etch commercially-relevant materials. A retarding field energy analyser is used to measure IEDFs, and on-wafer outcomes are investigated with a suite of metrology tools, including atomic force microscopy and scanning electron microscopy. The results are compared with radio-frequency biasing, showing the benefits of TWB for enhanced process control.

[1] Faraz, T., Verstappen, Y.G., Verheijen, M.A., Chittock, N.J., Lopez, J.E., Heijdra, E., van Gennip, W.J., Kessels, W.M. and Mackus, A.J., 2020. Precise ion energy control with tailored waveform biasing for atomic scale processing. *Journal of Applied Physics*, *128*(21).

2:45pm **AP+EL+MS+PS+TF-ThA-3 Precise Ion Energy Control Using Advanced Pulse Modulation for Thin Film Deposition and ALD**, ***Yejin Shin,*** WONIK IPS CO., LTD., Republic of Korea*; Junghoon Kim, Tae Cho,* WONIK IPS CO., LTD.*; Hyun-Joug Woo, YongBaek Jeon, GyuTai Kim, TaeJoon Kim,* WONIK IPS CO., LTD., Republic of Korea

As semiconductor device dimensions continue to shrink, advanced thin film deposition processes increasingly require precise control of ion energy and ion flux to achieve void-free filling in narrow-pitch and high aspect ratio structures. In particular, lateral gap-fill processes for next-generation semiconductor architectures demand highly controlled plasma-surface interactions to improve bottom coverage, suppress seam and void formation, and maintain film uniformity within confined geometries. Conventional RF plasma technology often provides limited flexibility for controlling ion bombardment conditions, motivating the development of advanced waveform engineering approaches.

In this work, an advanced pulse modulation was adapted to precisely control ion energy characteristics during RF plasma deposition processes through tailored voltage waveform. To enable this capability, the bottom components of a system were extensively modified, including the integration of a redesigned junction module and an optimized RF grounding architecture. The modified structure was specifically designed to improve transient voltage response, reduce parasitic effects, and support consistent pulse modulation under plasma load. Particularly, the hybrid junction module was designed to have minimized reflected power fluctuation and enabled more stable waveform delivery to the substrate electrode, which is critical for precise ion energy control during deposition processes. These hardware enhancements enabled more accurate control of sheath voltage evolution and allowed dynamic tuning of ion bombardment energy at the substrate surface. Using the developed platform, various pulse modulation conditions were investigated to evaluate their influence on plasma stability, ion energy distribution, and deposition characteristics. Experimental observations which were made using the advanced PEALD tool manufactured by Wonik IPS expects that advanced pulse shaping can significantly influence ion acceleration dynamics and plasma-surface interactions without substantially perturbing bulk plasma stability. In particular, the ability to manipulate transient sheath behavior enabled improved control of ion-assisted deposition compared with conventional continuous-wave RFs as a 13.56 or 27.1MHz.

This work establishes a hardware and process framework for future investigation of advanced deposition applications, focused on evaluating the effectiveness of this approach for next-generation conformal film deposition. The presented approach provides a promising pathway toward plasma processing for advanced semiconductor manufacturing applications requiring precise control of plasma-surface interactions.

3:00pm **AP+EL+MS+PS+TF-ThA-4 Characterizing Inductively Coupled Plasmas in Ar/N2/H2 Mixtures for Plasma Enhanced Atomic Layer Deposition of Crystalline Films**, ***David Boris,*** *Jeffrey Woodward, Virginia Wheeler, Michael Johnson, Mackenzie Meyer, Scott Walton,* U.S. Naval Research Laboratory

Low temperature plasmas containing mixtures of Argon, Nitrogen, and Hydrogen are widely used in the plasma enhanced atomic layer deposition of crystalline metal nitrides (e.g. AlN) at low temperatures (<500C).Generally, the addition of H_2 is beneficial in that it facilitates the removal of precursor ligands and leads to films with low carbon content (<1%). In addition, if the process conditions are properly chosen, highly crystalline metal-nitride films can be grown in $Ar/N_2/H_2$ mixtures.However, the effects of H_2 addition on the downstream plasma properties near the substrate are not well understood in remote, inductively coupled plasma (ICP) geometries.As such, a better understanding of the downstream plasma properties in this gas chemistry will be the focus of this presentation.

In this work, we use a combination of Langmuir probes, a retarding field energy analyzer, and optical emission spectroscopy (OES) to examine the effects of varying process parameters on the physical characteristics of $Ar/N_2/H_2$ plasmas generated in a remote, ICP geometry.In particular, a range of applied RF powers, gas flows, and pressures are explored with a focus on the resulting changes in atomic species density, plasma density, plasma potential, and the energy and flux of ions at the substrate.Of particular interest is the effect H_2 has on the ion flux and ion energy

distribution at the substrate. These changes in plasma properties are then tied to changes in the characteristics of AlN thin films grown via plasma-enhanced ALD using a remote ICP employing $Ar/N_2/H_2$ gas mixtures. This work was supported by the NRL Base program through the Office of Naval Research.

3:15pm **AP+EL+MS+PS+TF-ThA-5 Direct Atomic Printing of High-K Dielectric Thin Film Oxide Materials** *, **Tesfalem Welearegay**, Nandan Singh Ruhela, Simone Santucci, Mira Baraket, Maksym Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark

The rapid scaling up of CMOS microfabrication combined with growing demand for wide- and ultrawide-bandgap power electronics (GaN, SiC, β-Ga_2O_3), and the integration of high memory and neuromorphic devices have placed high-k dielectric thin films at the centre of modern semiconductor technology. High-k dielectric oxide thin films such as HfO_2, ZrO_2, Al_2O_3, Ta_2O_5, Nb_2O_5, and Ga_2O_3 are predominantly as-deposited by conventional atomic layer deposition (ALD) and spatial ALD techniques. Although ALD offers sub-nanometre control and excellent conformality, its low throughput, vacuum-based batch operation, high precursor consumption, and lack of in-line patterning have become major bottlenecks for the development and scale-up of next-generation high-k materials. These limitations become significant when device roadmap require sub-nm equivalent oxide thickness, and ultralow defect density to fine tune the film's intrinsic properties required for rapid materials screening with high throughput and precision..

We, therefore, present Direct Atomic Layer Processing (DALP®) technique — a spatial, atmospheric-pressure ALD technology platform that enables direct atomic printing of oxide thin films with monolayer-level precision and higher throughput while significantly reducing precursor waste. By spatially separating the precursor and oxidant zones under inert-gas exposures, DALP® technology combines the self-limiting surface chemistry of ALD with the speed and selective-area capability of a direct-write process. The platform offers unique versatility in fine-tuning the film composition, property and and structure, thereby enabling to control over the targeted properties of the film. The capability is demonstrated on two selected high-k oxide materials. GaOx deposited from its spatial precursor Galai™ (air liquide) with H_2O at relatively low temperatures of 150–240 °C under open atmosphere conditions. The as-deposited oxide films follows an ALD-like deposition window at 180–210 °C with growth per pass (GPP) of 0.35–0.5 Å/pass. Moreover, NbOx (Nb_2O_5) thin films were grown from its spatial precursor Nautilus 2™ (Air liquide) with H_2O at relatively low-temperature ALD window of 180 - 240 °C with GPP of 0.41 - 0.43 Å/pass, producing high-purity amorphous films suitable for different applications including DRAM capacitors, Mott memristors, and high-index optical coatings. These results establish DALP® technology as a versatile, sustainable, and high-throughput platform for the rapid development and manufacturing of high-k dielectric thin films for power electronics, memory, and quantum-device applications.

3:30pm **AP+EL+MS+PS+TF-ThA-6 Plasma-Enhanced ALD of $TaCxN_{1-x}$ Tailored for Superconducting Quantum Technologies Through Ion Energy and Other Plasma Control Knobs** *, **Silke Peeters**, Arthur De Jong, Adrie Mackus, Erwin Kessels,* Eindhoven University of Technology, Netherlands*; Harm Knoops,* Oxford Instruments Plasma Technology, Netherlands

Tantalum nitride compounds are emerging materials for superconducting quantum circuits due to their reduced surface oxidation compared to Ta, which is used in state-of-the-art devices. However, the synthesis of electrically conductive tantalum nitride compounds is challenging. Moreover, these circuits require sharp material interfaces with minimal impurities to achieve state-of-the-art performance.

Ar-H_2 plasma has enabled the preparation of superconducting TaC_xN_{1-x} through atomic layer deposition using the metalorganic $Ta[N(CH_3)_2]_3[NC(CH_3)_3]$ precursor. In previous work[1,2], we have shown that the quality of TaC_xN_{1-x} and $Nb_xTi_{1-x}N$ films can be substantially improved through ion-energy control, achieved via application of a radiofrequency (RF, 13.56 MHz) substrate bias during low-pressure, remote plasma exposure. In this work, we explore the novel method of tailored-waveform (TW, 200 kHz) biasing[3,4] and variation of the Ar-H_2 plasma composition to tune film properties for application in superconducting quantum devices.

Compared to RF biasing, TW biasing offers more precise control over the ion energy. Consistent with earlier RF-bias results, application of TW biasing up to an ion energy of 140 eV enhances grain growth and grain boundary quality through increased adatom mobility and preferential removal of weakly-bonded surface species. As a result, room-temperature electrical resistivity is improved from $(9.6 \pm 0.5)*10^4$ μΩ cm for an 11 nm film to $(3.8 \pm 0.2)*10^2$ μΩ cm for a 7 nm film. A decrease of the H_2-dilution in the Ar-H_2 gas mixture supplied to the plasma further enhances TaC_xN_{1-x} electrical conductivity and crystallinity, and promotes (111) texturing. A decrease in blistering, which can occur at high-stress, H-containing interfaces, is observed at the Si(100) substrate interface. The balance between Ar and H species significantly affects crystal grain growth. Ar species more effectively stimulate near-surface atomic rearrangement through physical bombardment, while H species act as reducing agents. However, H species can also reduce adatom mobility through over-passivation of dangling bonds and accumulate in the film.

This work shows that accurate understanding and control of plasma properties is necessary to tailor TaC_xN_{1-x} films to superconducting quantum technologies. Using the developed toolbox, we demonstrate successful integration of TaC_xN_{1-x} thin films in superconducting quantum technologies.

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3:45pm **AP+EL+MS+PS+TF-ThA-7 Direct Atomic Layer Processing (DALP®): Spatially Localized, Multi-Material Fabrication for Next-Generation Devices from Discovery to Manufacturing** *, **Mira Baraket**,* ATLANT 3D Nanosystems, Denmark

Progress in next-generation advanced electronic and functional devices, based on complex heterostructures and advanced materials integration, is increasingly constrained by the rigidity of conventional thin-film processing and patterning workflows. While these approaches deliver high material quality and uniformity, they offer limited flexibility for spatially localized, multi-material fabrication, three-dimensional thickness engineering, and rapid experimentation at the nanoscale within a single process flow.

ATLANT 3D introduces Direct Atomic Layer Processing (DALP®), a nanofabrication technology enabling digitally controlled, spatially localized deposition of multiple materials with atomic-scale precision. DALP allows different materials to be deposited sequentially and locally in a unified workflow, enabling manufacturing of complex material stacks, heterostructures, interfaces, and thickness gradients without intermediate lithographic patterning steps.

This presentation describes the DALP process architecture and its role in both combinatorial materials discovery and targeted device manufacturing for next-generation devices. By enabling programmable material placement, controlled thickness variation, and repeatable execution within a single platform, DALP supports accelerated materials exploration while also enabling the direct production of device-ready structures as part of broader manufacturing flows. Representative examples include multi-material nanoscale structures for advanced semiconductor and functional material applications, where precise interface control, spatial selectivity, repeatability, and manufacturability are critical. DALP expands the accessible design space of nanoscale fabrication and provides a a direct pathway from materials discovery to device-ready, manufacturable structures.

4:00pm **AP+EL+MS+PS+TF-ThA-8 From Plasma to Process: Understanding Dielectric Barrier Discharges for Spatial Atomic Layer Deposition** *, **Ralph Houben**, Antoine Salden, Jente Wubs, Richard Engeln, Erwin Kessels, Julian Held, Bart Macco,* Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) is a thin-film deposition technique based on sequential, self-limiting reactions. Plasma-enhanced ALD (PE-ALD) extends this concept by leveraging non-equilibrium plasmas to enable low-temperature processing, wider choice in materials, and enhanced film properties. Advancing PE-ALD requires a detailed understanding of plasma chemistry and the role of reactive species from the plasma in driving surface reactions.

Spatial ALD (SALD), in which precursor and reactant zones are separated in space rather than time, enables high-throughput and large-area processing, making it attractive for low-cost and high volume applications such as photovoltaics and batteries. SALD often operates at atmospheric pressure in linear slit geometries, making dielectric barrier discharges (DBDs) a natural plasma source. However, the high-pressure environment introduces strong collisionality that fundamentally alters plasma chemistry compared to low-pressure PE-ALD. For example, for O_2 plasmas, rapid three-body reactions favor ozone (O_3) formation over atomic oxygen (O). The gas temperature plays a crucial role here, as it directly affects the rate coefficients of the ozone-forming reactions. Furthermore, power dissipation occurs through filamentary microdischarges rather than a uniform glow —

both aspects that have no direct analogue in conventional low-pressure PE-ALD.

The oxidative species composition governs surface chemistry in oxide ALD. Quantifying O_3 and O with absolute densities — and linking them to plasma parameters through models — is essential for process control, yet such data for atmospheric DBDs in an ALD context are scarce.

In this work, ozone densities have been determined using broadband UV absorption spectroscopy, yielding absolute concentrations on the order of 10^{15} cm^{-3} under typical operating conditions. The density depends on dissipated power, gas temperature, and O_2 input in the gas mixture. We further present cavity ring-down spectroscopy (CRDS) as technique for probing the forbidden transition of atomic oxygen near 630 nm, providing calibration-free, absolute quantification of atomic oxygen densities. These measurements are supported by plasma chemistry modeling, which shows that the O_2/N_2 ratio governs whether ozone or atomic oxygen dominates — a critical distinction for ALD surface reactivity.

Furthermore, the species generation predicted by the model is directly tied to how power is dissipated in the discharge. Power dissipation analysis reveals the filamentary nature of the discharge and how it governs species generation. These insights are essential for rationally designing plasma-assisted SALD processes.

Spectroscopic Ellipsometry
Room 320 - Session EL-ThA

Spectroscopic Ellipsometry Oral Session

Moderators: Dr. Andy Antonelli, Antonelli Research and Technology, **Dr. Ufuk Kilic**, University of Nebraska - Lincoln, **Dr. Nikolas Podraza**, University of Toledo, **Prof. Dr. Eva Schubert**, University of Nebraska - Lincoln

2:15pm **EL-ThA-1 Spectroscopic Ellipsometry for Advanced Semiconductor Metrology Applications***, **Matthew Hilfiker**, Rostislav Grynko, Nick Keller,* Onto Innovation **INVITED**

Advanced logic and memory development continues to push device architecture well beyond the limits of traditional process control methods. As dimensions shrink and structures become increasingly complex, parameter correlation has increased, placing new demands on both metrology sensitivity and model robustness. While spectroscopic ellipsometry has long been a workhorse technique in semiconductor manufacturing, its effective use at advanced nodes requires broader spectral coverage, improved modeling approaches, and tighter control of measurement uncertainty.

This talk provides an overview of spectroscopic ellipsometry as it is applied to today's most challenging metrology problems. Measurements in the visible and ultraviolet remain critical for monitoring dimensional control at the atomic scale. At the same time, mid–infrared ellipsometry has emerged as an important complement, offering enhanced sensitivity to structural effects that are difficult to access at shorter wavelengths. Together, these capabilities allow metrology strategies to be tailored to the specific physics and correlations of a given process step.

As device architecture continues to evolve, improving metrology performance increasingly depends on combining advanced optical modeling with measurement approaches that remain stable across highly correlated parameter spaces. The role of rigorous coupled physical wave analysis (RCWA) enabling optical critical dimension analysis of complex three–dimensional structures will be discussed. The presentation will emphasize broader trends shaping spectroscopic ellipsometry as a critical enabler of advanced semiconductor manufacturing.

2:45pm **EL-ThA-3 In It to Thin It: Spectroscopic Ellipsometry for Native Oxide Measurement on Indium Thermal Interface Materials***, **Maxwell Junda**, Biswas Subedi,* Covalent

Native oxide layers on metal surfaces critically impact performance across industry. In semiconductor advanced packaging, native copper oxide at Cu-Cu hybrid bond interfaces can inhibit both electrical connectivity and bond integrity. For batteries, oxide on current collector foils influences interfacial impedance, and, for medical implants, surface oxide on titanium dictates biocompatibility and corrosion resistance. Here, we present the case of indium-based thermal interface materials (TIMs) where native oxide degrades wetting, thermal, and mechanical properties at the bond interface, contributing to void formation during reflow. Excessive oxidation can ultimately lead to thermal hot spots and reduced device reliability, making oxide thickness a key quality metric.

There are only a few metrology options for native oxides on metals. Being non-destructive, fast, and compatible with production inspection workflows makes spectroscopic ellipsometry (SE) appealing. The reality is, however, that topography, grain structure, and oxide composition variability on production surfaces present challenges for SE. Additionally, accuracy requires managing correlation between the oxide thickness and optical properties of both the metal and oxide in the optical modeling.

Covalent has developed a reliable SE-based native oxide thickness measurement on indium TIM surfaces. To overcome the inherent variability of commercial indium surfaces, we collect many distributed individual measurements to yield statistical distributions of oxide thickness. This ensures that locally anomalous sites do not overly bias the representative characterization of the overall oxidation level. Optical constants for both the indium metal and its native oxide were established through simultaneous multi-sample fitting across samples of varying oxidation, producing a robust model in which only oxide thickness remains as a fit parameter for routine inspection. Results were validated against both cross-sectional TEM and XPS. Oxide thicknesses for minimally oxidized samples are typically on the order of 5 nm. We also applied this methodology to compare as-received to intentionally oxidized samples, successfully discriminating oxide thicknesses relevant to TIM quality control. TIM shelf life was also studied through repeated measurements over time. This methodology is now deployed for routine indium TIM inspection.

Finally, we will discuss plans to extend this work with imaging ellipsometry to investigate oxide thickness variation at the microscale, to understand how surface topography and grain boundaries contribute to the spatial variability observed in focused-spot SE measurements.

3:00pm **EL-ThA-4 Developing an Optical Database of Thermally Evaporated Cadmium Selenide Telluride Alloys for Machine Learning Enhanced Spectroscopic Ellipsometry***, **Alex Bordovalos**, Nadeesha Katakumbura, Eva Mulloy, Bishal Shrestha, Suresh Chaulagain, Marie, Solange Tumusange, Balaji Ramanujam, Randy Ellingson, Ambalanath Shan, Nikolas Podraza,* University of Toledo

Machine learning techniques have shown great promise for performing rapid spectroscopic ellipsometry data analysis on simulated ellipsometric spectra in select case studies. It is critical that machine learning enhanced spectroscopic ellipsometry (MLSE) is applied to measured ellipsometric spectra collected for samples with varieties of layer structures to demonstrate its utility while developing a better understanding of transitioning MLSE from simulated ellipsometric spectra to measured ellipsometric spectra. To this end,the complex dielectric function ($\varepsilon = \varepsilon 1 + i\varepsilon 2$) spectra of thermally evaporated cadmium selenide telluride (CdSe(x)Te(1-x)) alloys are established for the purpose of simulating ellipsometric spectra that represent current fabrication techniques in CdSe(x)Te(1-x) photovoltaic (PV) devices.

A series of ten thermally evaporated CdSe(x)Te(1-x) alloys are deposited on commercial transparent conducting oxide glass. These alloys are measured with energy-dispersive X-ray spectroscopy to have Se content (x) of 0.00, 0.14, 0.25, 0.31, 0.36, 0.46, 0.62, 0.75, 0.85, and 1.00. A cadmium chloride (CdCl2) heat treatment, standard to PV devices, is applied to the alloys which are then measured with X-ray diffraction to reveal a wurtzite crystal structure at $x \geq 0.62$ and a zinc blende crystal structure at $x \leq 0.46$. Spectroscopic ellipsometry measurements are performed on these alloys. ε2 is determined using a background TaucLorentz oscillator, an Urbach tail, and a series of excitonic critical point parabolic band oscillators with common phase for a given crystal structure while ε1 is determined from analytically solving Kramers-Kroning integration and a Sellmeier expression. A set of polynomial fits are then applied to each optical property parameter to establish the variations of each parameter as a function of Se content. These relationships reduce the number of model fit parameters by mapping these optical property parameters to x.

This optical model for CdSe(x)Te(1-x) alloys is well suited for simulating ellipsometric spectra for the purposes of developing MLSE for CdSe(x)Te(1-x) PV applications because it has a comparatively smally number of parameters and the model generated optical properties are representative of materials in current devices. The next steps include training an MLSE model using simulated ellipsometric spectra and then applying the MLSE to measured ellipsometric spectra collected from CdSe(x)Te(1-x)PV device stacks.

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3:15pm **EL-ThA-5 Spectroscopic Ellipsometry Studies of Materials for High Power Electronics**, ***Madan Kumar Mainali***, *Prabin Dulal, Bishal Shrestha, Suresh Chaulagain, Venkanna Kanneboina, Ambalanath Shan, Nikolas Podraza,* University of Toledo

Wide band gap materials 4H-SiC and 6H-SiC are two hexagonal crystal polytypes of silicon carbide. It is used in high power electronics as it has high thermal conductivity, high operational temperature, higher efficiency with lower power loss, and high switching frequency. Spectroscopic ellipsometry is used to characterize the optoelectronic properties of 4H-SiC and 6H-SiC (0001) single crystal samples from MTI Crop, over the infrared (IR) to vacuum ultraviolet (VUV) (0.05 – 8.5 eV) spectral range. Spectroscopic ellipsometry is a non-contact optical characterization technique sensitive to structural (bulk film thickness, interfacial layer thickness, surface layer thickness), optical properties (band gap, above band gap transitions, phonon modes), and electronic transport (resistivity, carrier concentration, carrier mobility, scattering time, and carrier effective mass) properties. Complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra are obtained from reflection mode spectroscopic ellipsometry for backside roughened 4H-SiC and 6H-SiC. A single parametric model describing ε predominately for the ordinary directions is developed over the 0.05 – 8.5 eV for 4H-SiC and 6H-SiC with some contribution from the extraordinary direction of 6H-SiC in the IR region. Indirect band gaps for 4H-SiC and 6H-SiC are found to be 3.30 and 3.03 eV, respectively, and the corresponding direct optical gaps are at 4.46 and 4.42 eV. A model describing the optical response in the IR spectral range is created using a Drude expression with either transverse optical (TO) and longitudinal optical (LO) (TOLO) or Lorentz oscillator models. Free carrier concentration (N) is optically measured to be 3.7×10^{18} and 3.3×10^{18} cm^{-3} using TOLO and Lorentz oscillator models respectively, and the corresponding carrier mobility (μ) is 34 and 39 cm^2/Vs for 4H-SiC. For 6H-SiC, N is measured to 8×10^{18} cm^{-3} using either TOLO or Lorentz oscillator models and μ in the ordinary direction is 9 and 10 cm^2/Vs using the TOLO and Lorentz oscillator model, respectively, and 5 cm^2/Vs in the extraordinary direction using either model. For 4H-SiC, using the TOLO oscillator model, TO and LO phonon modes are obtained at 797.7 and 992.1 cm^{-1}, respectively. In 6H-SiC, TO modes in ordinary and extraordinary directions are found at 797.7 and 789.7 cm^{-1} and the corresponding LO modes are found at 992 and 984 cm^{-1}, respectively. The TO and LO modes obtained from the Lorentz oscillator model are consistent with modes obtained from TOLO model.

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3:30pm **EL-ThA-6 Photoacoustic Simulations for Acoustic Critical Dimension Metrology**, ***George Antonelli***, Antonelli Research & Technology; *Brian Daly,* Vassar College

Picosecond laser ultrasonics is a twenty year old high volume semiconductor metrology and continues to find new applications. One of the strengths of this technique is the deep connection between the development of the hardware and the multi-physics simulations that allow the extraction of critical parameters. As semiconductor devices continue their shift from 2D to 3D, analysis of photoacoustic data has become more challenging as the simulations are in general limited to planar stacks of films. The development of fast numerical methods for solving 3D light-matter interactions enabled the leap from films to structures giving birth to optical critical dimension (OCD) metrology.These numerical tools offer a template for a similar leap in photoacoustics. Acoustic critical dimension (ACD) metrology like OCD is an optical method, but it can non-destructively extract critical dimensions of 3D structures buried beneath an opaque surface. This method requires a new class of multi-physics simulation capable of performing tightly choreographed optical, electronic, and coupled opto-mechanical calculations. In this paper, previous work on this topic will be summarized and new algorithms realized in a software package under development will be presented. Two key components of this work are (1) the democratization of this complex analysis to facilitate its use by undergraduates and (2) a shift away from the structure definition as geometry found in OCD today and towards a process driven paradigm. Structures are therein defined by the way they are manufactured and fits on the structures can be linked back to the fundamental process parameters.

3:45pm **EL-ThA-7 Optical Modeling of Plasmonic Nanostructures**, ***Peter Petrik***, *Géza Szántó, Deshabrato Mukherjee, Chao Zeng, Máté Stift, Shayesteh Raeisi, Zoltán Lábadi,* Centre for Energy Research, Hungary; *Attila Bonyár,* Budapest University of Technology and Economics, Hungary; *Miklós Fried,* Centre for Energy Research, Hungary

Plasmonic nanostructures are utilized in many applications for sensing, photonics, and much more. General models in ellipsometry that focus on transfer matrix, effective medium, first principle oscillators, and analytical dispersion functions show difficulties when modeling such structures. In this work we present modeling approaches and applications for characterizing a broad variety of plasmonic and periodic nanostructures, including gratings, nanoparticles created by annealing, electrochemistry, as well as combinatorial sputtering. The formation of nanoparticles was monitored during annealing and electrochemistry. We utilized both through-liquid and Kretschmann-Raether cells for monitoring the growth of gold layers in an electrochemical cell, as well as the interaction between silk layers and analytes in Kretschmann configurations. We also studied the adsorption of flagellar filaments on nanostructured gold surfaces and their electrochemical sensing performance. The optical sensing properties of periodic gold nanostructures were also investigated in terms of measuring the ambient and thin overlayers, as well as the sensitivity for the determination of the dimensional parameters of the periodic structures. Using simplified hemispherical numerical models, we explained the sensing performance of annealed gold layers created by combinatorial sputtering. The sensitivity as a function of the initial amount of deposited gold and type of analyte was measured and explained by numerical finite element modeling of the gold nanostructures and adsorbed layers.

4:00pm **EL-ThA-8 Engineering Anisotropic Optical Properties in Hybrid Plasmonic Metamaterials**, ***Ufuk Kilic***, *Raymond Smith, Yousra Traouli,* University of Nebraska-Lincoln; *Christos Argyropoulos,* Pennsylvania State University; *Eva Schubert, Mathias Schubert,* University of Nebraska-Lincoln

Hybrid plasmonic metamaterials provide a powerful platform for tailoring light–matter interactions through structural control of their effective dielectric properties [1-3]. Here, we investigate the anisotropic optical response of bottom-up engineered Si–Ag hybrid plasmonic metamaterials fabricated using glancing angle deposition (GLAD). Sequential oblique-angle depositions combined with controlled substrate rotation enable deterministic control of nanocolumn geometry, optical anisotropy, and structural handedness over large areas [2-3]. The optical properties are characterized using Mueller matrix generalized spectroscopic ellipsometry (MM-GSE) from the near-infrared to the ultraviolet spectral range. Multi-layer anisotropic effective-medium approximation analysis is employed to extract the wavelength-dependent dielectric tensor elements and quantify the influence of plasmonic–dielectric hybridization on the effective optical response. The extracted dielectric functions reveal pronounced anisotropy and strong tunability arising from the engineered morphology, material composition, and structural handedness of the nanocolumn architectures.

Finite-element-method simulations are performed to establish the physical origin of the observed optical behavior. The simulations reveal strong polarization-dependent field localization and spin-dependent plasmonic mode coupling, producing enhanced optical anisotropy and broadband chiroptical activity, including pronounced circular dichroism extending from the near-infrared to the ultraviolet. Excellent agreement between experiment and theory validates the extracted dielectric functions and effective-medium analysis. **Complementary high-resolution imaging, crystallographic analysis, and compositional characterization, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD), confirm the formation of spatially coherent, compositionally distinct, and morphologically uniform hybrid nanocolumn arrays.**The combined experimental and theoretical investigation establishes a framework for engineering anisotropic dielectric functions in hybrid plasmonic metamaterials through nanoscale structural design. The demonstrated tunability of the effective dielectric response provides opportunities for polarization-selective photonics, broadband chiral platforms, optical sensing, and integrated nanophotonic technologies.

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4:15pm **EL-ThA-9 From Disordered Nanoparticles to Periodic Gratings: A Unified Framework for High-Precision Plasmonic Metrology**, ***Deshabrato Mukherjee**, Géza Szántó, Chao Zeng, Máté Stift, Shayesteh Raeisi, Zoltán Lábadi,* Centre for Energy Research, Hungary*; Attila Bonyár,* Budapest University of Technology and Economics, Hungary*; Miklós Fried, Peter Petrik,* Centre for Energy Research, Hungary

We developed a high-throughput screening and ultra-sensitive detection framework using two distinct architectures: a disordered graded gold nanoparticle platform for rapid process optimization and periodic gold gratings for predictable accurate performance.

The high-throughput combinatorial platform was created by depositing graded gold layers (0-20 nm) along the X-axis on fused silica using magnetron sputtering, followed by annealing up to 600°C. This led to the formation of self-assembled nanoparticles with laterally varying surface density from 2090 to 88 particles/μm^2, resulting in an evolution of morphology from oblate to hemispherical. This was followed by spatially resolved operando tracking using a modular Avantes fiber optic scanning spectroscopy system that mapped the transition of the localized surface plasmon resonances and volatile vapor pathways. The finite element method (FEM) calculations were modeled using JCMsuite to analyze nanoparticle formation and near-field properties. To detect ethanol, water layers via Peltier cooling, and chemisorbed MBA monolayers, we isolated specific thickness thresholds from 1.6 to 3.2 nm as the optical sensing regimes. These findings were evident due to the localized geometry and the near-field coupling due to the inter-particle gaps resulting in a surface-enhanced Raman spectroscopy (SERS) enhancement factor of 10^6 under confocal laser excitation.

Complementing this, we developed periodic gold gratings using a non-destructive metrology framework. The periodic gold gratings (CD between 70-130, thickness 60 nm, and period 200 nm) were fabricated using electron-beam lithography and reactive ion etching. These grating parameters were chosen for fabrication after multi-dimensional FEM simulations using JCMsuite to determine the changes or variations in the amplitude ratio represented by Ψ and the phase difference represented by Δ of the polarized reflection coefficients. The gratings were measured in reflection-mode with Woollam M-2000DI spectroscopic ellipsometer and fitted, and complemented with FEM modeling that enhances the traditional effective medium approximations. We demonstrated that the phase-sensitive parameter, Δ, provides superior sensitivity over the amplitude parameter, Ψ simulating across a five-dimensional parameter space that included the critical dimensions, period, thickness, wavelength, and angle of incidence. Using structural partial derivatives, we achieved a bulk refractive index limit of detection of 10^{-5} refractive index units, a critical dimension uncertainty in the picometer range, and a surface mass density limit of detection of 10 pg/mm^2 using De Feijter overlayer modeling.

Atomic Scale Processing Mini-Symposium
Room Ballroom A - Session AP+EL+PS+TF-ThP

Atomic Scale Processing Mini-Symposium Poster Session

AP+EL+PS+TF-ThP-1 Design of Gas Flow Field for a Slip Flow ALD Processing Chamber, ***Kyung-Hoon Yoo***, Korea Institute of Industrial Technology, Republic of Korea; *Geun-Soo Song,* The KUMYOUNG Inc., Republic of Korea; *Chun-Sik Kim,* TNG Co., Republic of Korea; *Jun-Young Hwang, Sang-Ho Lee, Jeong-Jin Kang, Shin-Ae Song, Kyung-Tae Kang,* Korea Institute of Industrial Technology, Republic of Korea; *Hyeong-Cheol Lee,* Hanyang University, Republic of Korea; *Kun-Hyung Lee,* SAMSUNG DISPLAY, Republic of Korea

As semiconductor feature sizes reach the nanometer scale, ALD processing equipment has become indispensable for atomic-layer control. However, conventional ALD processes face significant challenges regarding economic and environmental feasibility due to the excessive consumption of precursors and energy.[1,2] To address these issues, it is essential to establish sustainable manufacturing technologies through the development of high-efficiency ALD processing chambers. In the present study, we propose a slipflow based ALD chamber designed to optimize the process space and minimize resource waste. The nitrogen flow fields within the chamber were numerically investigated using Computational Fluid Dynamics (CFD) for process gap sizes of 1, 10, and 100 mm at 400 °C. Under an inlet static pressure of 1 Torr and a mass flow rate of 4.233×10^{-5}kg/s, the Knudsen number (Kn) and flow Reynolds number (Re) were evaluated as 0.0137 and 0.822, respectively for the 10 mm gap. These values confirm that the flow resides within the slip flow regime, where rarefaction effects at the surface wall become significant. Accordingly, the steady-state compressible laminar flow field was simulated by solving the continuity, momentum, and energy equations.[3,4]

Acknowledgment

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AP+EL+PS+TF-ThP-2 Nucleation and Evolution of Dislocations and Extended Faults in Complex Perovskite Oxides, ***Rishi Raj***, *K. Andre Mkhoyan,* University of Minnesota, USA

The stoichiometric flexibility of a perovskite oxide (ABO_3) results in several unique properties due to the presence of three elements in the crystal structure. This allows it to host a variety of defects across all dimensions. 1D primitive edge dislocations with varying terminations, screw dislocations as well as 2D structural faults like Ruddlesden-Popper, elastic distortions, and BO_3 octahedral tilts are commonly observed and studied. Even though structure and electronic properties of some of these defects have been reported, the nucleation and growth of such defects and dislocations is still unclear. Analytical STEM study of perovskite oxide thin films of $BaSnO_3$ and $SrSnO_3$ show the existence of two kinds of edge dislocations: single ([001]/(100)-type) and dissociated ([001]/(110)-type) edge dislocation each with two half planes missing. Six different types of such dislocations are possible and observed due to the terminations of the perovskite half planes. Similarly, 2D Ruddlesden-Popper faults are also observed to result from missing planes of atoms, suggesting a correlation with 1D dislocations. Apart from such conventional topological defects, complex perovskite oxides also showcase several line defects and dislocations with reconstructed cores. This suggests we can selectively populate the material with defects by altering the terminations of crystal half planes. Strain tuning during growth by swapping substrates or decorating the surface morphology can effectively allow termination control. This would allow certain defect and dislocation structures to be more favorable than others. By establishing this correlation between 1D and 2D faults, this work provides a potential pathway to transition from passive extended defect management to intentional, termination-controlled defect engineering.

AP+EL+PS+TF-ThP-3 Atomistic Study of the Effect of Moisture-Modified Amorphous SiO_2 Interfaces on Gas-Phase Clustering in LPCVD, ***Minseung Cha***, Seoul National University, Republic of Korea

Particle formation is a critical issue in LPCVD processes because nanoscale contaminants can cause film defects, pattern failure, yield loss, and process instability. Although particle generation is often explained by precursor decomposition and homogeneous gas-phase reactions, the chemical state of quartz-glass components used in LPCVD equipment has not been sufficiently considered. In particular, amorphous SiO_2 surfaces are widely exposed in parts such as process tubes, chambers, boats, injectors, and nozzles, and these surfaces can be modified by moisture during air exposure.

In this study, we investigate the role of moisture-modified amorphous SiO_2 interfaces in gas-phase clustering using molecular dynamics and density functional theory calculations. Dry SiO_2, hydroxylated SiO_2 surface models are constructed to represent different surface states. H_2O adsorption and dissociative chemisorption are first examined to evaluate silanol formation. The interaction between reactive molecules or cluster precursor species and each SiO_2 surface is then analyzed in terms of adsorption stability, residence behavior, and desorption tendency.

We propose that hydroxylated SiO_2 surfaces can act as reactive boundaries rather than inert walls in LPCVD environments. Surface silanol groups may temporarily stabilize reactive species through hydrogen bonding and electrostatic interactions, increasing local molecular concentration near the interface. These stabilized species can subsequently return to the gas phase and enhance molecular aggregation, thereby increasing the probability of cluster and particle formation.

This study provides an atomistic interpretation of how the moisture exposure condition of quartz-glass parts can influence gas-phase clustering in LPCVD processes. The results suggest that controlling moisture exposure and the hydroxylation state of amorphous SiO_2 interfaces in components such as nozzles, chambers, and boats may be important for particle suppression and process stability.

Keywords: LPCVD, amorphous SiO_2, H_2O vapor, hydroxylation, silanol, molecular dynamics, MD, density functional theory, DFT, gas-phase clustering, particle formation, quartz glass, semiconductor, process

AP+EL+PS+TF-ThP-4 Low Temperature Atomic Layer Deposition of ZnO for Optoelectronic Applications, ***Anil Yadav***, *Aditya Sadhanala,* Indian Institute of Science, India

This work demonstrates the ultra-low-temperature atomic layer deposition (ALD) of ZnO thin films at 50 °C and 70 °C using a 1 M diethylzinc (DEZ) solution in hexane and water as precursors. This was achieved in a custom-built ALD chamber with precise control over the process parameters. Despite the ultra-low deposition temperatures, the resulting ZnO films demonstrated excellent uniformity. This approach not only solves the problem of substrate compatibility by enabling ultra-low-temperature growth but also demonstrates the use of solvent-diluted pure precursors. The X-ray diffraction (XRD) patterns of as-deposited ZnO films deposited at 50 °C and 70 °C as a function of the number of ALD cycles from 50 to 250 were measured. As the ALD deposition cycles increased to 100, distinct diffraction peaks corresponding to (100), (002), and (101) planes emerged. When the deposition temperature increased from 50 °C to 70 °C, the (002) peak became more intense and sharper, indicating improved crystallinity.

To evaluate the electronic properties of ZnO thin films deposited at ultra-low temperatures of 50 °C and 70 °C, we integrated them as the active layer in field-effect transistors (FETs). The fabricated devices demonstrated exceptional electrical characteristics, exhibiting an I_{ON}/I_{OFF} ratio exceeding 10^8 with the saturation mobility of 0.85 cm^2/V.s. These results clearly confirm the applicability of solution-based precursors for ultra-low-temperature ALD depositions in electronic device applications.

AP+EL+PS+TF-ThP-5 Oxidation-Assisted SF_6 Remote Plasma Etching for Surface Roughness Reduction of TiN, ***Min Kyun Sohn***, *Subin Heo, Seong Hyun Lee, Sun Kyu Jung, Jeong Woo Park, Dongwoo Suh,* Electronics and Telecommunications Research Institute, Republic of Korea

Titanium nitride (TiN) is widely used as a conductive diffusion barrier and work-function metal in advanced semiconductor devices. As device dimensions continue to scale down, controlling not only the etch amount but also the post-etch surface morphology becomes increasingly important, because nanoscale roughness can directly affect electrical reliability,

interface quality, and subsequent film deposition. In the present study, we investigate the effect of SF_6 remote plasma-based etching on the surface morphology of TiN thin films, with particular emphasis on the role of a pre-oxidation step.

Three TiN surface conditions were compared: as-deposited TiN, TiN exposed to SF_6 radicals only, and oxidized TiN followed by SF_6 radical exposure. The etch per cycle (EPC) increased from 0.16 Å/cycle for the SF_6-only process to 0.38 Å/cycle for the oxidation-assisted SF_6 radical process, indicating that surface oxidation enhanced the fluorine-radical-driven removal of TiN. Atomic force microscopy measurements showed that the as-deposited TiN exhibited an RMS roughness of 1.313 nm, which modestly decreased to 1.117 nm after direct SF_6 radical exposure. In contrast, when the TiN surface was oxidized prior to SF_6 radical exposure, the RMS roughness further decreased to 0.850 nm, corresponding to an approximately 35% reduction compared with the as-deposited TiN surface, demonstrating a clear surface-smoothing behavior.

This difference suggests that the oxidation step plays a critical role in modifying the TiN surface before fluorine-radical exposure. The smoothing behavior is attributed to the formation of a TiO_x or TiO_xN_y surface layer during oxidation, followed by its conversion into volatile TiF_x species during SF_6 radical exposure. The higher EPC and lower RMS roughness obtained after oxidation-assisted SF6 exposure suggest that the modified surface layer can be removed more efficiently and uniformly than the native TiN surface. This oxidation-assisted pathway provides a chemically controlled route for reducing TiN surface roughness without relying on ion-driven physical sputtering.

These results indicate that surface pre-oxidation can be an effective strategy for controlling the morphology of TiN during radical-based etching. The proposed oxidation-assisted SF_6 radical process offers a potential strategy for morphology-controlled TiN etching in nanoscale device integration.

AP+EL+PS+TF-ThP-6 Development of in-Situ Laser Diagnostics Measurements of CH_3 Radical Concentrations for Study of Thin Film Depositions Using Organo-Metallic Precursors, ***Mruthunjaya Uddi***, Advanced Cooling Technologies Inc.*; Prawal Agarwal, Devon Jensen,* ACT*; Anatoli Morozov,* Princeton University*; Arthur Dogariu,* Texas A&M University

Many environmentally friendly non-halogen precursors contain CH3 structure component. Plasma chemical vapor deposition of pure metallic thin films using these precursors is challenging and requires better understanding of the gas phase and surface reaction mechanisms. We present a novel, time and spatially resolved, in-situ femtosecond laser diagnostics method to measure CH3 radicals in a non-equilibrium plasma environment. The CH3 radicals are predissociated to CH2 and H radicals using a 275 nm femtosecond laser pulse, followed by a 205 nm probe beam to measure the H radical concentrations. A single femtosecond laser is used to generate the required 275 nm and 205 nm beams. Measuring and knowing the dissociation cross section of CH3 radical by 275 nm pump beam, allows the quantification of CH3 radical concentrations with spatial and time resolution.

AP+EL+PS+TF-ThP-7 Hybrid Electrospun ZnO Nanofiber and ALD ZnO Electron Transport Layers for Near-Infrared Organic Photodiodes, ***Anna Leonard***, *Neha Chaturvedi, Veena Misra,* North Carolina State University

Organic photodiodes (OPDs) require efficient electron transport layers (ETLs) to achieve charge-selective extraction while minimizing recombination and dark current impacts. In this work, hybrid ZnO ETLs consisting of electrospun ZnO nanofibers and atomic layer deposited (ALD) ZnO were investigated for integration into near-infrared OPDs with a PTB7-Th:IEICO-4F active layer. The inclusion of the electrospun ZnO nanofibers increases the interfacial area between the ETL and active layer and provides enhanced electron transport pathways while the ALD ZnO layer provides film continuity and assists in passivating traps to mitigate defect states introduced by the nanofibers.

Three ETL architectures were investigated: ZnO fibers beneath ALD ZnO, ZnO fibers above ALD ZnO, and ALD ZnO control devices. ZnO nanofibers were fabricated through electrospinning of a zinc acetate dihydrate/polyvinylpyrrolidone (PVP) solution followed by calcination to oxidize the fibers and remove excess PVP. Device performance was evaluated through dark current density vs. voltage (J_{Dark}-V) and external quantum efficiency (EQE) measurements. Devices utilizing hybrid nanofiber/ALD ZnO ETLs exhibited reduced initial dark current compared to control devices indicating suppression of leakage pathways and trap-assisted recombination. Enhanced EQE response was observed in devices with fibers deposited above the ALD ZnO layer, suggesting improved interface quality and charge extraction.

These results demonstrate that combining electrospun ZnO nanostructures with ALD ZnO provides a promising method to engineer ETLs for high-performance OPDs and other optoelectronic devices.

AP+EL+PS+TF-ThP-8 Site-Specific and Temperature-Dependent Hydration of Faceted Hematite, ***Asare Dua***, Illinois Institute of Technology*; Luke Pretzie,* Purdue University*; Ashley Bielinski,* Argonne National Laboratory*; Yue Li,* Argonne National Lab*; Valentine Novosad, Cong Liu, Alex Martinson,* Argonne National Laboratory*; Adam Hock,* Illinois Institute of Technology

Alpha hematite (α-Fe_2O_3) is an abundant metal oxide whose surfaces and interfaces control key processes in catalysis, sensing, and photoelectrochemistry. While the more stable α-Fe_2O_3 (001) surface is well studied, less stable facets such as (012) and (104) which are more relevant in the aforementioned applications due to higher surface activity remain least studied. Surface sites of α-Fe_2O_3 (012) and (104), as well as their distinct stability were identified through temperature-dependent hydration by combining in situ infrared reflection absorption spectroscopy (IRAS) with density functional theory (DFT) vibrational analysis. For α-Fe_2O_3 (012), we found sites that promoted the dissociative and molecular adsorption of D_2O. Dissociatively adsorbed D_2O were either terminal or bridging. In both cases the hydroxyls were either isolated or interacting with nearby species. Protons of bridging hydroxyls (μ3a-OD (isolated); μ3b-OD (interacting with nearby hydroxyls)) are bound to triply coordinated surface oxygens while terminal hydroxyls (μ1a-OD (interacting with nearby hydroxyls)) were bound to octahedral surface Fe atoms (Fe_{oct}^{3+}). Similar to dissociatively adsorbed D_2O, molecularly adsorbed D_2O was either isolated (D_2Oa) or interacting with nearby hydroxyls (D_2Ob). α-Fe_2O_3 (104) on the other hand exhibited an isolated doubly coordinated bridging hydroxyl (μ2a-OD) and an interacting bridging species (μ2b-OD) rather than triply coordinated bridging hydroxyls. This preference is backed by our DFT calculations which shows triply coordinated bridging hydroxyls were highly unstable on α-Fe_2O_3 (104). Results from IRAS showed two isolated terminal hydroxyls, μ1a-OD and μ1b-OD, were present on the surface of α-Fe_2O_3 (104). This indicates two types of undercoordinated surface atoms existed with the first being undercoordinated tetrahedral Fe atoms (Fe_{tet}^{3+}) since they're the surface atoms of α-Fe_2O_3 (104), while the second is from the second layer of Fe atoms which have octahedral geometry. The undercoordination of Fe_{oct}^{3+} atoms however suggests oxygen vacancies (V_o) were present and some of these might migrate from surface to the second lattice of α-Fe_2O_3 (104). Our temperature dependent studies support this hypothesis since the population of μ1a-OD, μ1b-OD, and μ2a-OD increased with increasing temperature when under vacuum (0.8 torr). The distinct local environments of the sites on α-Fe_2O_3 (012) and α-Fe_2O_3 (104) and changes in properties with respect to temperature revealed through this work provide a fundamental tool that may be used to engineer the surface of alpha hematite through site- or facet-selective atomic layer deposition.

Spectroscopic Ellipsometry
Room Ballroom A - Session EL-ThP
Spectroscopic Ellipsometry Poster Session

EL-ThP-1 Optical Properties of Metal Thin Films Measured by Spectroscopic Ellipsometry, ***Kathryn Brown***, *Suresh Chaulagain, Prabin Dulal, Mohammed Alaani, Ambalanath Shan, Nikolas Podraza,* University of Toledo

As the race for higher and higher efficiency photovoltaic (PV) cells accelerates, device simulation has gone from a niche theoretical tool to an absolute necessity. In order to make these simulations as accurate as possible, it is vital to have well understood optical properties for each layer in the device. One such layer which is often overlooked is the metal back contact.

This work investigated the optical properties of three common back contact materials, namely Copper, Silver, and Gold. Thin films of each metal were deposited on fused silica glass. All three films studied were of a nominal thickness such that they appear functionally infinite to the instrument. Samples were measured by variable angle spectroscopic ellipsometry (VASE) in the range from 0.031-5.87 eV and at three separate angles of incidence, 50°, 60°, and 70°. Data from two separate instruments were combined to achieve this range. The resulting data were analyzed using the Sellmeier method to create Kramers–Kronig consistent parameterized

models for each material. Properties interpreted from these results include complex refractive index ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and surface roughness.

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EL-ThP-2 Engineering the Optimal Filter: Nonlinear Noise-Reducing Filters in Spectroscopy, ***David Aspnes,*** North Carolina State University*; Long Le,* Vietnam Academy of Science and Technology, Viet Nam*; Young Kim,* Kyung Hee University, Republic of Korea

In previous work, we assessed linear filters used in spectroscopy, which operate by attenuation. Here, we assess nonlinear filters, which operate by replacement. By eliminating apodization errors, these nominally outperform linear filters but require some level of modeling. In direct (spectral) space (DS) this takes the form of replacing all or part of the data with least-squares-fit model lineshapes. In reciprocal- (Fourier-) space (RS), the equivalent is least-squares-fitting model coefficients to the low-order coefficients dominated by information, then replacing the higher-order data coefficients dominated by noise. The RS approach is new, and required appropriate mathematical functions to be developed. This generalizes RS filtering, because the only previous approach, the corrected-maximum-entropy (CME) method, can be applied only to spectra that are positive-definite and have no dispersion character. In RS filtering the option also exists to retain some of the low-order data coefficients, an advantage for complicated spectra.

Using false-data calculations, we rank filters in order of performance. If a model is known to represent a spectrum accurately, the best filters are DS lineshape-fitting and its RS counterpart. The next best are the partial-replacement RS noted above, and, in situations where it can be applied, the CME. As expected, apodization errors relegate linear filters to last place, although they have the advantages of simplicity and not requiring modeling.

Finally, our calculations show unequivocally that the fundamental limit of any filter, linear or nonlinear, to extract information from spectra is the inability to separate information from low-order noise. Examples are provided.

EL-ThP-3 Optical Properties of CrN Measured by Spectroscopic Ellipsometry, ***Farihatun Jannat Lima,*** *Alexander Bordovalos, Suresh Chaulagain, Ambalanath Shan, Nikolas Podraza,* University of Toledo*; Dilara Sen, Olivia Fairlamb, Frank Peiris,* Kenyon College*; Duc V. Dinh, Xiang Lü, Oliver Brandt,* Paul-Drude-Institut für Festkörperelektronik, Leibniz-Institut im Forschungsverbund Berlin e.V., Germany

Chromium nitride (CrN), a transition-metal nitride, has attracted attention in the field of electronics and energy as resistive coatings due to its excellent mechanical characteristics. It also has intriguing electronic, magnetic, and thermoelectric properties. In this work, an epitaxial (111) oriented CrN film deposited on Al2O3 (0001) is measured by spectroscopic ellipsometry over a spectral range from 0.031 to 5.877 eV to extract complex optical properties and bandgap energy using a rotating compensator Fourier transform infrared (IR) ellipsometer (FTIR-VASE, J.A. Woollam Co.) and a single rotating compensator multichannel ellipsometer (J.A. Woollam Co. M-2000) from the near IR to ultraviolet. Divided spectral range analysis is performed to determine structural parameters and thicknesses and initial sets of optical properties described by physically realistic models in the respective spectral ranges. The weakly absorbing photon energy range from 0.3 to 0.734 eV is initially ignored to prevent model-dependent bias in the vicinity of the bandgap. From the structural model, it is determined that CrN surface is optically less dense than the bulk of the thin film. Numerical inversion is performed over the full measured spectral range to determine the complex dielectric function ($\varepsilon = \varepsilon1 + i\varepsilon2$) spectra of CrN. The numerically inverted ε spectra in the full measured range is parametrized using a Kramers-Kronig consistent model. Three transverse optical (TO) phonon modes are observed at 387 cm-1, 403 cm-1 and 1048 cm-1. Three corresponding longitudinal optical (LO) phonon modes are identified from the loss function ($-1/\varepsilon$) at 596 cm-1, 622 cm-1 and 871 cm-1. The absorption coefficient (α) is determined from numerically inverted spectra in ε. Tauc plots of $(\alpha h\nu)2$ and $(\alpha h\nu)1/2$ as functions of photon energy reveal a direct gap energy of 0.815 eV and an indirect gap energy of 0.56 eV.

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EL-ThP-4 Optical and Structural Properties of Sbxsey Thin Film Co-Evaporated via Elemental Sources, ***Bishal Shrestha,*** *Mohammed Razooqi Alaani, Madan Mainali, Alisha Adhikari, Balaji Ramanujam, Prabin Dulal, Venkanna Kanneboina, Ambalanath Shan, Nikolas Jacob Podraza,* University of Toledo

Antimony selenide (Sb_2Se_3) is low cost, highly stable, low toxicity, high radiation tolerant, and earth abundant semiconductor with established applications in photodetectors, batteries, and memory device technologies. In recent years, it has emerged as a promising photovoltaic absorber owing to its high visible light absorption coefficient ($>10^5$ cm^{-1}), quasi one-dimensional structure favoring charge transfer, and an optimal band gap (1.1 – 1.3 eV). Although the current record power conversion efficiency for a single-junction Sb_2Se_3 solar cell stands at 10.57% with a theoretical limit of ~32%, further performance gains are primarily limited by the persistent challenge of achieving high-quality, phase-pure, and stoichiometric Sb_2Se_3 thin films. Owing to substantial disparity in vapor pressures between Sb and Se during deposition, conventional chemical and physical deposition techniques requiring precursor Sb_2Se_3compounds result in thin films with compositional deviations, secondary phases, and elevated defect densities, requiring additional treatments to lower the degree of imperfections. Hence, for photovoltaic device applications, an ideal fabrication and characterization technique must be developed to obtain optimized films with the appropriate optical, structural, morphological, and compositional properties. With this motive, our approach employs thermal co-evaporation of elemental Sb and Se sources, enabling improved stoichiometric control of Sb_xSe_y thin films through independent regulation of source temperatures. For material characterization, particular emphasis is placed on in-situ and ex-situ spectroscopic ellipsometry analysis to investigate evolution of optical response and structural parameters in the as-deposited to post-deposition annealed states of the films. Our study of complex dielectric function spectra over an extended spectral range from 0.03 eV (mid-infrared) to 5.87 eV (ultraviolet) is the first documented experimentally derived data for this material. These comprehensive optical data will serve as valuable resource for device simulation across broad spectral range to explore material's further potential, whereas the optical/structural parametric expression developed here can be applied to investigate similar materials regardless of fabrication technique. Scanning electron microscopy, energy dispersive spectroscopy, and x-ray diffraction measurements are used to compare the morphological, compositional, and crystallographic characteristics of the as-deposited and annealed thin films.

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EL-ThP-5 Composition-Dependent Optical Properties of Silver-Aluminum Alloy: An Ellipsometric Approach, *Jonas Sikah,* ***Will Cusak,*** *Alexander Kozen, Matthew White,* University of Vermont

Semitransparent metal thin films have been widely used in optoelectronics because of their excellent optical and electrical properties. Among such, silver (Ag) is commonly employed due to its excellent conductivity and low optical losses in the visible range. In addition, introducing a minor fraction of Al into Ag facilitates the formation of smooth thin films by decreasing the percolation threshold of pure Ag. However, the optical properties of these Ag-Al alloy films fails to represent the weighted average of optical properties of their independent metal counterparts. Therefore, we present a detail ellipsometric investigation of the optical properties of Ag-Al alloy thin films deposited on glass substrates using vacuum thermal evaporation. The alloy compositions were tailored by adjusting deposition rates to achieve Ag volume fractions ranging 100% to 0% while Al volume fractions ranging from 0% to 100%.The film thicknesses of all compositions of Ag-Al alloys were kept at 100 nm. Scanning electron microscope (SEM) images confirmed the smooth film formation when Al content is higher in the alloy film. Energy-dispersive X-ray spectroscopy confirmed the compositional variation, with atomic percentages tracking the intended volume fraction. Spectroscopic ellipsometry was conducted at room temperature across 200 – 1000 nm at incident angles of 500, 550, and 600. The complex refraction index (n) and dielectric function (k) were extracted using model-based fitting employing Bruggeman effective medium approximations.Within the UV–Visible spectral range, increasing the Ag concentration resulted in a reduction of n values, while a progressive increase in Al content led to an enhancement of n in Ag–Al alloy thin films. At near-IR to IR region, films with higher Ag content exhibited higher n values while increasing Al content systematically reduced the n values exhibiting a trend typical of metallic films due to the decreasing contribution of free electrons response. The k values followed a constant trend thoughtout the UV-Visible-IR range with a lower k values with higher Ag content and higher k values with lower Ag content in the Ag-Al alloy. These findings demonstrate the tunablity of

optical behavior linked to alloy compositions which can be applied to plethora of optoelectronic devices accordingly.

EL-ThP-6 iCVD Parameters with Structural and Dielectric Properties of Hydrophobic and Hydrophilic Polymer Thin Films: A Multi-Sample Spectroscopic Ellipsometry Analysis, ***Parvez Amin Khan***, *Hamidreza Mohajeri, Ufuk Kilic,* University of Nebraska - Lincoln*; Mathias Schubert,* University of Nebraska-Lincoln*; Siamak Nejati,* University of Nebraska - Lincoln

Unlike the conventional Chemical Vapor Deposition (CVD) process, initiated CVD (iCVD) offers a unique, solvent-free pathway for synthesizing conformal polymeric thin films. Their tailored chemical functionality such as hydrophilicity, hydrophobicity, and lipophobicity polymer thin films have been utilized in several technological applications including photocatalytic applications, sensors, organic LED, and solar cells. In this study, we provide a comprehensive investigation on the wettability characteristics of iCVD grown Polytetrafluoroethylene (PTFE) and poly glycidyl methacrylate (pGMA) thin films. We focused on their hydrophobic and hydrophilic performances and correlated them to their optical and material properties. The pGMA and PTFE thin film samples were fabricated at 350°C on silicon wafer with a deposition rate of 7.89 nm/min and 8.26 nm/min respectively. The relationship between deposition parameters (filament temperature, monomer flow rates) and material and structural properties of fabricated thin films (thickness, roughness, surface energy) were identified using spectroscopic ellipsometry techniques, X-ray photoelectron spectroscopy and the wettability characteristics of fabricated thin films were extracted from contact angle (CA) measurements. Moreover, Multi-Sample Approach based spectroscopic ellipsometry data analysis provides the dielectric function of the fabricated films across the near-infrared (0.72 eV) to vacuum ultraviolet (6.4 eV) spectral range. Cauchy dispersion model with Urbach absorption tail is employed for extracting parametrized optical properties of thin films. We found that while the optical properties remain identical for different thickness of the fabricated polymers, we observed an increase in the roughness from 21.97nm to 38.04nm with the increase in thickness from 29.32nm to 123.86nm of the thin films. For PTFE, the increase in roughness also results in enhanced hydrophobic characteristics as we observed 18% increase in the CA of drop cast DI water with increase in the thin film thickness. For pGMA, we also increase the thickness from 95nm to 118nm, however the roughness layer thickness was not changing. From the CA measurements, we found that unlike pTFE, pGMA exhibit hydrophilic characteristics and the increase thickness did not change wettability due to the surface morphology remain unchanged and the constant surface energy profile of this polymer kind. This finding shows the importance of surface profile in wettability characteristics of thin films which are critical in the advancement of surface engineering pathways.

EL-ThP-7 Optical Properties of Boro-aluminosilicate Glass using Spectroscopic Ellipsometry from 0.079 to 5.89 eV, ***Eva Mulloy***, *Prabin Dulal, Suresh Chaulagain, Emily Amonette, Alex Bordovalos, Ambalanath Shan, Nikolas Podraza,* University of Toledo

Boro-aluminosilicate glass has high mechanical strength and chemical durability and is used widely in a variety of applications, including liquid crystal display substrates, glass fibers, thermal shock-resistant glass containers, and radioactive waste glasses. A commercially available boro-aluminosilicate glass is optically characterized by reflection mode spectroscopic ellipsometry and unpolarized transmittance over the infrared (IR) through the ultraviolet (UV) spectral range. Ellipsometric spectra (N, C, S) are collected using a near IR to UV rotating compensator spectroscopic ellipsometer from 0.73 to 5.89 eV (M-2000FI, J. A. Woollam Co.) and one further extended in the IR from 0.032 to 0.73 eV (IR-VASE, J. A. Woollam Co.) each at 50°, 60°, and 70° angles of incidence. A continuous parameterization of complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra is developed from 0.079 to 5.8 eV. The parameterization of ε for this glass consists of a constant additive term to ε_1 (ε_∞), a Sellmeier expression, and Gaussian oscillators. A transfer-matrix-based numerical inversion of unpolarized transmittance spectra provides enhanced sensitivity to weak absorption from the UV to the near IR region. Parameters defining absorption features in numerically inverted ε_2 are fixed, and parameters only impacting ε_1 are fit to produce a final parametric model. From ε, distinct infrared vibrational modes can be linked to specific bonding configurations, while the onset of ultraviolet absorption arises from electronic transitions and defect states within the glass network. Sensitivity to relatively strong features at 1379, 1040, 745, and 332 cm^{-1} is obtained from ellipsometry, and transmission can resolve weaker features at 1782, 2710, and 3541 cm^{-1}.

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EL-ThP-8 Birefringence of GdScO3 using Transmission Spectroscopic Ellipsometry, ***Prabin Dulal***, *Balaji Ramanujam, Nikolas Podraza, Ambalanath Shan,* University of Toledo

Gadolinium scandate ($GdScO_3$) is an emerging material with potential applications in advanced electronics and photonics primarily due to its interesting electronic, magnetic, and optical properties. It crystallizes as a perovskite-type oxide with an orthorhombic crystal structure, exhibiting a high dielectric constant, thermal stability, and large band gap energy. This study investigates the optical properties of a commercially available single crystal, double-sided polished $GdScO_3$ sample with a (110) Miller index surface plane orientation. The birefringence of the sample was derived using Mueller matrix spectroscopic ellipsometry (SE) over a spectral range of 280 nm to 1650 nm.

A full set of Mueller matrix data were obtained using an ellipsometer in straight-through mode with the sample at normal incidence. The fast axis of the biaxial sample was aligned with respect to the transmission axis of the polarizer in the generation arm of the ellipsometer. The measured matrix elements show no discernible dichroic effects, and the off-diagonal elements are virtually zero, implying that the sample exhibits properties of an ideal compensator. The measured lower right block Mueller matrix element data, composed of pure sinusoidal functions of retardance, shows oscillatory behavior with respect to spectra, consistent with a compensator with high retardance due to the thick (~ 0.54 mm) sample being evaluated. The lower right matrix elements also show a steady attenuation in the oscillatory data, beginning around 600 nm and approaching zero around 350 nm. Since there is no significant absorption in this region, we attribute this to depolarization resulting from incoherence due to the interaction of multiple beams within the thick sample with the finite bandwidths of the ellipsometer's source and detector.

To determine birefringence, the measured lower right Mueller matrix elements, for a spectral range greater than 400 nm, were first deconvolved from polarization-dependent attenuation. Next, because the order of the retardance is undetermined due to the relative thickness of the sample, there is ambiguity over the true retardance value determined from the deconvolved matrix elements. To address this, a model-based approach in which an extended Cauchy model with four fit parameters was employed to model the birefringence. Fit parameters were generated using the Monte Carlo approach, and the Levenberg-Marquardt algorithm was used to fit the relevant matrix element data to experimental data while minimizing mean squared error between datasets.

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Atomic Scale Processing Mini-Symposium
Room 316 - Session AP1+EL+PS+TF-FrM

Thermal and Plasma-Enhanced ALD

Moderators: Dr. Sagar Udyavara, LAM Research, **Dr. Virginia Wheeler**, U.S. Naval Research Laboratory

8:15am **AP1+EL+PS+TF-FrM-1 Analyzing Plasma-Enhanced ALD of III-Nitrides via Experimental and Theoretical Studies***, Steven Allaby, Heba Saleh, Fatih Bayansal,* ***Necmi Biyikli,*** University of Connecticut **INVITED**

Research efforts on low-temperature (T < 300 ℃) synthesis of crystalline III-nitride thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early III-nitride growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to stainless-steel based hollow-cathode plasma sources revealed highly (002) oriented polycrystalline III-nitride films on Si(100) and sapphire substrates. Upon further modification of the hollow-cathode plasma source and reactor chamber design, we have achieved monocrystalline AlN, quasi-epitaxial GaN and (002) oriented InN films on sapphire substrates at a common growth temperature of 200 ℃.

The films were deposited using conventional metal-alkyl precursors (trimethylaluminum, triethylgallium, trimethylindium) and various nitrogen plasmas (N_2/H_2/Ar, N_2/H_2, N_2/Ar, and N_2-only) as metal precursor and nitrogen co-reactant, respectively. *In-situ* ellipsometry and optical emission spectroscopy (OES) were employed to monitor the surface ligand-exchange reactions, plasma surface interactions, and formed reaction byproducts in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness variation, growth-per-cycle (GPC) and optical properties of the III-nitride films. When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for III-nitride films on c-plane sapphire substrates showed a notable increase. Moreover, a significant improvement of crystalline order has been observed for all binary nitride films grown on sapphire substrates, achieving or approaching epitaxial quality films. We attribute this significant improvement in crystal quality to the synergistic impact of customized HCP-ALD reactor, large-diameter third-generation hollow-cathode plasma source, and optimized growth conditions (plasma gas mixture, rf-power, pressure).

To gain further insight into how different plasma mixtures and radical species affect III-nitride film quality, we have carried out density functional theory (DFT) based simulations of both metal-organic and plasma half cycles. The computational studies revealed how different adsorbed metal-organic precursor surface groups interact with hydrogen and nitrogen radicals by depicting energetically favorable reaction routes. These results are compared and correlated with the experimental observations, deciphering the critical role of hydrogen radicals.

8:45am **AP1+EL+PS+TF-FrM-3 Optical Bandgap and Thermal Stability Driven High–κ Engineering of HfAlO Dielectrics on a 200 mm ALD Platform***, Partha Mukhopadhyay, Zuriel Caribe, Ivan Fletcher, Jim Fulford,* Tokyo Electron America, USA

This work demonstrates the tunable high–κ, optical, and thermal stability characteristics of hafnium aluminate ($Hf_xAl_{1-x}O$) thin films synthesized using a 200 mm high–volume batch atomic layer deposition (ALD) platform. Precise monolayer–level engineering of HfO_2/Al_2O_3 superlattice structures enables controlled Al incorporation, which systematically modulates the optical bandgap, dielectric constant, and electrical structure of the alloy. A key outcome is that increasing Al content systematically increases the optical bandgap of the alloy from 5.5 – 6.5 eV, accompanied by improved film density and structural uniformity, which directly influences the dielectric response and reliability of the material.

At lower Al content (~0.31), the alloy exhibits superior dielectric properties with κ > 22 and a capacitance density of 12.46 fF/μm^2, representing ~29% enhancement over HfO_2, attributed to suppressed oxygen vacancies and reduced trap density. With increasing Al composition, the widened bandgap increases barrier height, resulting in reduced leakage current and improved dielectric robustness. A higher Al fraction (~0.56) demonstrates a breakdown electric field of ~8 MV/cm, exceeding HfO_2 by over 3 MV/cm, while maintaining low leakage (~10^{-6} A/cm^2) even after 650 ℃ annealing. Notably, increasing Al content significantly enhances the thermal budget of the dielectric stack, stabilizing the amorphous phase and preventing dielectric degradation at elevated temperatures, while preserving relatively high κ values compared to pure Al_2O_3.

XPS analysis reveals systematic shifts of Hf4f and Al2p peaks toward higher binding energies with increasing Al concentration, indicating modified bonding characteristics and enhanced ionic contributions, consistent with bandgap widening and improved film stability. These electronic structure changes correlate with reduced surface charge transfer effects and improved dielectric integrity. Additionally, the films exhibit excellent capacitance linearity over applied voltage and stable frequency response, making them highly suitable for RF applications.

The 200 mm batch ALD platform ensures excellent uniformity, repeatability, and scalability for compositionally engineered dielectrics. Overall, this study highlights that Al–content–driven optical bandgap tuning, coupled with improved thermal stability and enhanced breakdown strength, provides a powerful route to customize high–κ behavior in HfAlO. This enables optimized performance trade–offs between capacitance density, leakage, and reliability, making HfAlO a compelling material system for advanced MIM capacitors in BEOL, RF, and memory technologies.

9:00am **AP1+EL+PS+TF-FrM-4 Atomic Layer Deposition Metal and Barrier Layers Enabling Next Generation Interconnects***, Matthew Weimer, Sara Harris,* Forge Nano*; Thomas Moffat,* NIST-Gaithersburg*; Dane Lindblad,* Forge Nano*; Daniel Josell,* NIST-Gaithersburg*;* ***Arrelaine Dameron,*** Forge Nano

Device miniaturization continues to push the technological boundaries of manufacturing processes and integrated circuit (IC) manufacturing must keep pace to meet the design requirements for next-gen transistors. Back end of line (BOEL) fabrication poses several challenges to chip scaling: most notoriously the copper bottleneck in which thick barrier layers and resistance capacitance (RC) delays limit functional interconnect pitch to 21 nanometers [1]. To overcome this critical barrier, low resistivity, conformal metal films have been studied for hybrid metallization; decreasing interconnect resistance and reducing barrier layer thicknesses. As interconnect pitch decreases line-of-sight PVD copper barrier/seed layers experience pinch off and void formation [2]. This work explores the use of ruthenium (Ru) and lower resistivity thermal ALD iridium (Ir) thin films for copper seed layers to enable next generation interconnects. Thermal ALD Ir and Ru deposited at 250 ℃ both demonstrate conformal deposition on 10:1 aspect ratio through glass vias (TGVs) and show void free copper fill using a cyclic pulsed electrochemical deposition process. Deposited in partnership with ALD SiO2 and TiN layers, this completes a metal barrier seed solution for TSVs. As expected, the primary difference between the Ir and Ru is electrical resistivity. Seed film resistivity as deposited on TGVs was measured using four-point probe; a 10 nm Ru film measured 41 μΩ·cm and a 10 nm Ir film measured 16 μΩ·cm. Successful copper electrochemical deposition (ECD) at various ECD potentials, was completed with 10 nm of Ir with (resistivity 16 μΩ·cm) and 20 nm of Ru (resistivity 22 μΩ·cm) with the full layer stack for these film shown in Figure 1. Reduction in required layer thickness combined with improved electrical properties and demonstrated conformality can serve as crucial steps forward for advanced interconnects and BEOL architecture. Additionally, this work compares Ir film quality as deposited at 250 ℃ and 300 ℃. Ir deposited at 300 ℃ exhibits improved environmental stability when compared to 250 ℃ Ir as measured with 4-point probe after aging in atmosphere over several months. 300 ℃ Ir also shows a shortened nucleation delay, and optical constants (n and k) more closely aligned to bulk Ir values, as measured with spectroscopic ellipsometry. Ir film characterization for both temperatures including XPS, XRR, XRD and AFM is ongoing, and will be presented

9:15am **AP1+EL+PS+TF-FrM-5 Tuning the Mechanical Properties of Silica Aerogels Using Atomic Layer Deposition***,* ***Victor Vogt,*** *Ali Madanchi, Katherine Rybkin, Andrés Miranda Mañón, Andrej Lenert, M.D. Thouless, Neil Dasgupta,* University of Michigan

Silica aerogels are a key material used in aerospace, catalysis, and energy applications due to their ultralow density and thermal conductivity as well as high solar transparency. Specifically, they show promise as an emerging transparent insulating material in concentrating solar thermal energy generation.[1] In our recent work we have shown that atomic layer deposition (ALD) can be used to improve the thermal stability of silica aerogels at high temperatures of up to 800 ℃.[2,3] This was attributed to the ability of ALD to conformally modify the pore structure of the aerogels and form a more thermally stable phase at the surface. However, silica aerogels also suffer from low strength and fracture toughness, restricting their potential applications and making practical implementation difficult due to the risk of brittle fracture in assembly or operation.

In this study, we utilize sub-nanometer ALD treatments to conformally modify silica aerogels with aspect ratios > 100,000:1. We demonstrate a monotonic increase in stiffness with increasing number of ALD cycles, resulting in a ~30-fold increase in elastic modulus after 3 cycles of Al_2O_3 (nominal ~4 Å thickness). This result is investigated using finite element modeling (FEM) of the aerogel nanostructure, which reveals the key factors which drive the large increase in elastic modulus. Furthermore, we show that ALD increases the fracture toughness of the aerogels, resulting in a ~7-fold increase in fracture toughness after 3 ALD cycles. Due to the ultra-thin and conformal nature of the ALD layer, the porous nanostructure is maintained, allowing the aerogels to maintain high solar transparency and low thermal conductivity. This method enables a pathway to broader applications for silica aerogels through improving their mechanical durability while maintaining the favorable properties of low thermal conductivity and high optical transparency over a range of operating temperatures.

References:

[1] McEnaney, K., Weinstein, L., Kraemer, D., Ghasemi, H. & Chen, G. Aerogel-based solar thermal receivers. *Nano Energy* **40**, 180–186 (2017).

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

[3] Z.J. Berquist, A.J. Gayle, N.P. Dasgupta, and A. Lenert, Transparent Refractory Aerogels for Efficient Spectral Control in High-Temperature Solar Power Generation. *Adv. Funct. Mater.* **32**, 2108774 (2022).

9:30am **AP1+EL+PS+TF-FrM-6 Multilayer FUV Coatings Using ALD-Grown LaF_3 and ZrF_4, *John Hennessy,*** Jet Propulsion Laboratory

We report on the targeted development of atomic layer deposition processes for high-refractive-index metal fluorides, specifically focusing on lanthanum fluoride and zirconium fluoride. The primary objective is to integrate these ALD-deposited materials into multilayer optical coatings designed for demanding far-ultraviolet (FUV) applications. By successfully combining ALD processes for lanthanum and zirconium fluorides with established processes for lower-index materials, we enable the fabrication of specialized optical components that are critical to various NASA applications. As a demonstration of this ALD capability, a 16-layer AlF_3/LaF_3 mirror was fabricated and shown to achieve an average reflectance exceeding 90% within a band centered around 140 nm. Finally, we discuss the prospects for increasing coating complexity and further optimizing FUV performance.

9:45am **AP1+EL+PS+TF-FrM-7 Controlling the Crystallinity of V_2O_5 Deposited by Plasma-Enhanced Atomic Layer Deposition*, Scott Walton,*** *Peter Litwin, Neeraj Nepal, Maria Sales, David Boris, Michael Johnson, Mackenzie Meyer, Virginia Wheeler,* Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) 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 to ALD generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce amorphous, crystalline, and epitaxial films of varying types and characteristics. Importantly, by carefully controlling the plasma properties, it has been shown that the degree of crystallinity and phase selection is possible.

In this work, we demonstrate the ability to manage the crystallinity of V_2O_5 through careful control of the plasma characteristics during growth in a Kurt J. Lesker 150 LX PEALD system. We employ both plasma diagnostics and material characterization techniques to understand the process-to-structure-property relationship while varying the input power, operating pressure, and gas flow ratio. Optical emission spectroscopy (OES) and Langmuir probe measurements are used to characterize the production and delivery of energetic and reactive species to the growing film surface, while x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are used to characterize the physico-chemical properties of the V_2O_5 films. We find that by varying the operating pressure in the system during the plasma process, the films can be selectively deposited in an amorphous or crystalline state. We link the transition from amorphous to crystalline material to the energy flux density delivered to the material surface during deposition and derive an estimate of the critical energy flux density necessary for crystallization. Lastly, we discuss these results more broadly and the applicability of these findings to other material systems. This work is supported by the Naval Research Laboratory base program.

10:00am **AP1+EL+PS+TF-FrM-8 Epitaxial Growth of VN on Si_3N_4(0001)/Si(111) Using Molecular Beam Epitaxy*, Nuri Oncel,*** *Mehmet Ozdogan, Carlos Munoz, Deniz Cakir,* University of North Dakota*; Randy Duma,* Quantum Design*; Rajendra Dulal,* University of North Dakota

We report on the epitaxial growth of VN thin films on β-Si_3N_4 (0001)/Si(111) substrates using molecular beam epitaxy. The growth process and resulting film properties were systematically investigated using in-situ reflection high-energy electron diffraction (RHEED) and ex-situ scanning/transmission electron microscopy (S/TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive spectroscopy (EDS), and electrical transport measurements. RHEED and cross-sectional TEM analyses confirm the formation of epitaxial VN(111) films, with growth proceeding via a Volmer–Weber Island mechanism followed by coalescence. Increasing nitrogen flux during deposition significantly improves film continuity, stoichiometry, and crystalline quality. Structural characterization reveals an azimuthally aligned epitaxial relationship without the expected in-plane rotational reconstruction, indicating that interfacial bonding and strain relaxation dominate over simple lattice-mismatch considerations. XPS and EDS measurements confirm near-stoichiometric VN composition with reduced oxygen incorporation at higher nitrogen flux. Electrical measurements demonstrate ohmic transport across the VN/Si_3N_4/Si heterostructure, suggesting efficient carrier transport through the ultrathin dielectric layer via tunneling or defect-assisted conduction. Low-temperature transport measurements reveal a suppressed superconducting transition temperature relative to bulk and oxide-supported VN films, attributed to compressive strain and structural disorder. These results establish Si3N4(0001)/Si(111) as a viable platform for integrating epitaxial VN with semiconductor technology and provide insight into nitride–nitride heteroepitaxy and interface-driven property modulation.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP2+EL+PS+TF-FrM

Enabling Atomic Scale Processing (ALD/ALE) by leveraging new Precursors and Surface Reactions

Moderators: Prof. Austin Minnich, California Institute of Technology, **Dr. Angel Yanguas-Gil**, Argonne National Laboratory

10:30am **AP2+EL+PS+TF-FrM-10 Plasma-Enhanced ALD of SiO_2 with an Alternative Precursor: From Mechanistic Insight to Area-Selective Deposition*, James Jensen,*** *Jay Swarup, James Engstrom,* Cornell University

Silicon dioxide (SiO_2) is and has been an extremely important thin film material in microelectronics and related fields.The great majority of approaches to atomic layer deposition (ALD) of SiO_2 involve the use of plasma since, for example, the Si-H bond is resistant to reaction with molecules such as H_2O and O_2.We have examined the use of an alternative Si precursor, which we refer to as di-isopropylamido trisilylamine [DiPA(TSA)], employing an O_2 plasma as the co-reactant. The precursor contains only Si-N and Si-H bonds.We have investigated the process using *in situ* real time quartz crystal microbalance (QCM) techniques in a custom-built hot-wall reactor, which provides detailed insight into the half-reactions, and the presence of nucleation delay.We find that ALD with DiPA(TSA) occurs over a large temperature window, spanning a range of T = 120 – 285°C.The thickness deposited per cycle decreases with increasing temperature, from 4.7 Å-cycle^{-1} at T = 120°C to 2.9 Å-cycle^{-1} at T = 285°C.These rather large rates of growth from ALD reflect the silicon content in the precursor (three atoms per molecule).From QCM a nearly complete loss of the di-isopropylamido ligand is implicated in the precursor half reaction.The deposited thin films have been characterized using *ex situ* X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR), spectroscopic ellipsometry (SE) and atomic force microscopy (AFM).From XPS we find that the thin films are near stoichiometric (O:Si ~ 1.9) over the entire range of temperatures, while the expected impurities (e.g., C, N) are < 1%.From XRR we find that the thin film density increases from 2.24 g-cm^{-3} at T = 120 °C, to 2.38 g-cm^{-3} at T = 285 °C, which can be compared to the values for amorphous silica (2.20), and quartz (2.65).From AFM we find that the thin films are continuous and smooth exhibiting an average roughness of 0.54 nm at T = 120 °C (19 nm thick film), and 0.30 nm at T = 285 °C (13 nm thick film).Finally, we have conducted a preliminary set of studies concerning blocking PE-ALD growth of SiO_2 on Al_2O_3 using acetylacetone

(Hacac) and we find the deposition can be blocked for at least 10 cycles, over the temperature range *T* = 120-285 °C.

10:45am **AP2+EL+PS+TF-FrM-11 Temperature-Dependent Growth Behavior of Aluminum Oxide Using Dimethylaluminum Isopropoxide and Water**, ***Azeez O. Musa,*** University of Missouri-Columbia*; Hemant Kumar, Campbell Sweet,* University of Missouri, Columbia*; Justin R. Walensky,* University of Missouri-Columbia*; Matthias J. Young,* University of Missouri, Columbia

Area-selective atomic layer deposition (AS-ALD) requires precursors with controlled surface reactivity to enable selective film growth on targeted regions while minimizing unwanted nucleation on non-growth surfaces. Dimethylaluminum isopropoxide (DMAI) has emerged as a promising alternative to trimethylaluminum (TMA) for AS-ALD applications due to its reduced reactivity and non-pyrophoric nature. However, experimental mechanistic studies of DMAI/H_2O ALD and the influence of deposition temperature on growth behavior remain limited. In this work, the temperature-dependent growth characteristics of Al_2O_3 ALD using DMAI and H_2O were investigated using in situ quartz crystal microbalance (QCM) measurements together with ex situ X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and spectroscopic ellipsometry. DMAI was synthesized from aluminum isopropoxide and trimethylaluminum in 79% yield and >95% purity, with product formation confirmed by ^{1}H NMR spectroscopy. Real-time QCM measurements were used to examine precursor adsorption, ligand removal behavior, saturation conditions, and mass gain per cycle (MGPC) between 100 and 200 °C. Al_2O_3 growth at 100 °C exhibited a lower MGPC (~19 ng cm^{-2} cycle^{-1}) and less stable saturation behavior compared to films deposited between 150 and 200 °C, where the average MGPC remained approximately constant at ~29 ng cm^{-2} cycle^{-1}. Single-cycle QCM analysis further revealed distinct differences in surface reaction behavior between low- and intermediate-temperature growth regimes. These findings provide experimental insight into DMAI/H_2O ALD surface chemistry and establish growth conditions relevant to the development of DMAI-based AS-ALD processes.

11:00am **AP2+EL+PS+TF-FrM-12 Void-free Thermal ALD BaTiO3 Thin Films Prepared by Removing Water Dose after Ba Precursor**, ***Jiayi Chen,*** Georgia Institute of Technology, China*; Mark Losego,* Georgia Institute of Technology, USA*; Asif Khan,* Georgia Institute of Technology

This talk will discuss our efforts to develop a robust atomic layer deposition process (ALD) to create ferroelectric $BaTiO_3$ (BTO) thin films using Bis-(1,2,4 triisopropylcyclopentadienyl)-Barium and Titanium Isopropoxide precursors.Ferroelectric materials are potential candidates for future low voltage RAM and NAND memory because of their reversible two polarization states under low external electric field. While the CMOS compatible gate dielectric materials HfO_2 and $Hf_{0.5}Zr_{0.5}O_2$ are ferroelectric, they have high coercive fields that make it difficult to lower switching voltages below 1 V. Therefore, perovskite ferroelectric materials, like $BaTiO_3$ are desirable to use for these applications because their coercive voltages can be an order of magnitude lower, approaching 0.1 V.However, these ferroelectric films must be deposited by ALD to match the conformality and small thickness requirements desired for RAM and NAND memory. While reports exist for ALD processes of these materials, most if not all those reports use ALD recipe of “A metal precursor – oxidant – B metal precursor – oxidant”. This talk will present our finding that high quality BTO films can still be deposited with recipe in the form of “H_2O – Ba – Ti” or “H_2O – Ba – Ba – Ti”. A hypothetical ALD chemistry mechanism is proposed. These reactions can happen at 280 °C, but not 220 °C. Inverting the precursor sequence, such that H_2O – Ti – Ba, does not work. XRD confirms the formation of BTO crystal lattices through these novel recipes. One benefit of these recipes is getting void-free BTO films after annealing, whereas our previous studies show that conventional ALD recipes produce BTO films with voids because of the evaporation of H_2O during annealing. 40 nm BTO film deposited with this dehydration recipe shows high dielectric constant of 72 with low dielectric loss at the magnitude of 10^{-3}.

11:15am **AP2+EL+PS+TF-FrM-13 Optimizing Molybdenum Pentachloride Delivery for Vapor Deposition Processes**, ***James Maslar,*** *Vladimir Khromchenko, Berc Kalanyan,* NIST-Gaithersburg

Molybdenum metal has favorable properties for ultrathin layers compared to metals such as copper and tungsten and, therefore, has attracted much recent interest as a potential material for interconnects and gate metallization. A common method for forming ultrathin metal layers in high volume manufacturing is vapor deposition. For vapor deposition of molybdenum metal layers, molybdenum pentachloride is a common precursor. However, molybdenum pentachloride is a solid and can be difficult to reproducibly deliver from the precursor canister to the deposition surface in a tool, depending on delivery conditions and canister design. Also of concern is the presence of molybdenum oxychloride impurity species in the canister, and whether the oxychlorides are being generated during delivery or are present in the supplied material. The primary goal of this study was to characterize the process space for pulsed delivery of molybdenum pentachloride with respect to overall mass carryover, pulse-to-pulse stability, and impurity evolution. The approach used in this study was to quantify the amount of molybdenum pentachloride and molybdenum oxychlorides in an argon carrier gas as a function of carrier gas flow rate, system pressure, canister temperature, and canister design. Quantification was based on direct absorption measurements in the ultraviolet-visible and infrared spectral regions. The results of this study should facilitate the identification of process conditions that optimize molybdenum pentachloride for different applications.

11:30am **AP2+EL+PS+TF-FrM-14 Atomic Layer Modulation of Ru-Ir Alloy Thin Films for Low-Resistivity Interconnect Applications**, ***Yoonseo Choi,*** *Wonjoong Kim, Byungchan Lee, Minhyeok Lee, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

As semiconductor devices continue to scale down, Ru and Ir have attracted attention as promising candidates to replace Cu interconnects because their short mean free path and low bulk resistivity lead to a low figure-of-merit (FOM). However, ALD-grown single Ru and Ir thin films suffer from increased resistivity at thicknesses comparable to their mean free path due to enhanced electron scattering, particularly surface scattering, and film discontinuity. In this study, a Ru-Ir system was designed and fabricated by atomic layer modulation (ALM) to mitigate the thickness-dependent resistivity. ALM sequentially exposes different precursors to the surface with purge steps between each precursor exposure, followed by co-counter reactant exposure, enabling multicomponent thin films growth within a single atomic-layer cycle. In particular, the ratio of each element is controlled by the surface reactivity, adsorption behavior, and steric hindrance effects of the precursors, making ALM advantageous for forming compositionally uniform Ru-Ir alloy thin films even at reduced thicknesses. In this work, Ru-Ir alloy thin films were deposited at 250 °C by sequentially pulsing tricarbonyl(trimethylenemethane)ruthenium ($Ru(TMM)(CO)_3$) and tricarbonyl (1,2,3-η)-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ($C_{18}H_{27}IrO_3$) as Ru and Ir precursors, respectively, with O_2 as the counter reactant. To design the process and understand the composition-control mechanism, density functional theory (DFT) and Monte Carlo (MC) simulations were used to analyze precursor surface reactions and their effects on film composition. In addition, a deep-learning-based framework (IDEAL) was used to explore candidate compositions and crystal structures for Ru-Ir alloy films. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses confirmed that ALM-grown Ru-Ir films formed a solid solution without distinct phase separation. The electrical properties varied depending on the alloy composition; while single Ru and Ir films showed resistivity above 40 μΩ·cm at 7 nm, Ir-rich Ru-Ir films exhibited a relatively low resistivity of 37.6 μΩ·cm at 5 nm. The high crystallinity of the Ir-rich Ru-Ir films was also consistent with the IDEAL framework prediction. These results demonstrate that ALM-based Ru-Ir alloy thin films can overcome the thickness-scaling limitations of single-component Ru and Ir thin films and have potential as next-generation interconnect materials for replacing Cu.

11:45am **AP2+EL+PS+TF-FrM-15 Pulsed Thermal Etching of Amorphous TiO_2 Thin Films Using $MoCl_5$**, ***Hyuenwoo Yang,*** National Institute for Science and Technology (NIST)*; James Maslar, Berc Kalanyan,* NIST-Gaithersburg

Gas-phase pulsed etching has emerged as a promising approach for advanced thin-film processing, enabling controlled and potentially low-damage material removal with advantages in process integration over conventional continuous etching methods. Despite growing interest in pulsed etching, including atomic layer etching (ALE), the thermal etching chemistry of metal halides—particularly $MoCl_5$—remains largely unexplored for oxide materials. In this work, we investigate the pulsed thermal etching of amorphous TiO_2 thin films by $MoCl_5$ in a warm-walled viscous-flow reactor. Thickness changes were monitored in real time by in-situ spectroscopic ellipsometry during repeated $MoCl_5$/Ar cycles, while delivered precursor dose and impurity content were monitored upstream using a non-dispersive UV–vis gas analyzer.

Amorphous TiO_2 films on Si/native SiO_2 exhibited clear thickness loss under repeated $MoCl_5$ exposure, with etching behavior that depended strongly on substrate temperature, $MoCl_5$ source temperature, and Ar purge duration. Increasing the $MoCl_5$ source temperature increased the measured UV–vis

absorbance signal and produced a corresponding increase in TiO_2 etch rate, indicating that precursor delivery is a key parameter controlling the etching behavior. A substrate-temperature-dependent process window was also observed: etching was strongly suppressed at 150 °C and 350 °C, while the highest etch rate was observed near 250 °C. Temperature-switching experiments further showed that the low-temperature suppression was reversible upon heating to 250 °C, whereas exposure at 350 °C led to an etch-inactive state that did not recover after returning to 250 °C.

To our knowledge, this is the first report of TiO_2 etching using pulsed $MoCl_5$ chemistry. This work establishes an initial process window for $MoCl_5$-based thermal oxide etching and identifies precursor dose, substrate temperature, delivery history, and purge duration as important variables governing pulsed TiO_2 etching.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index