adsorbing $(CH_2OH)_2$+HF, as well as $(CH_2OH)_2$ adsorbed layers on SiO_2 surfaces, may be tested in future experiments.

Atomic Scale Processing Mini-Symposium
Room Ballroom BC - Session AP-ThP
Atomic Scale Processing Poster Session

AP-ThP-2 Thermal Atomic Layer Etching of Lanthanum Oxide Using Acetylacetone and Ozone, ***Aziz Abdulagatov****, Jonathan Partridge,* University of Colorado at Boulder*; Charles Dezelah,* ASM Microchemistry Ltd., Finland*; Steven George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of lanthanum oxide (La_2O_3) was demonstrated using sequential exposures of acetylacetone (Hacac) and ozone (O_3). Hacac reacts with La_2O_3 by a ligand addition and hydrogen transfer reaction to form volatile $La(acac)_3$ and H_2O according to: La_2O_3 + 6Hacac → $2La(acac)_3$ + $3H_2O$. Ozone was then used to remove carbon residue resulting from Hacac exposure on the surface.

In situ spectroscopic ellipsometry (SE) was used to monitor the film thickness change with number of ALE cycles. SE observed the linear decrease of La_2O_3 film thicknesses versus number of Hacac and O_3 cycles. Semicrystalline La_2O_3 thin films displayed etch rates of 0.2, 0.4 and 0.69 Å/cycle at 230, 250 and 270 °C, respectively. The SE studies also showed that the Hacac and O_3 surface reactions were self-limiting.

Atomic force microscopy (AFM) analysis of semicrystalline La_2O_3 on Si with a thickness of 20 nm displayed surface smoothing versus ALE cycles.The RMS surface roughness was 3.3 Å prior to ALE and 0.9 Å after ALE. Quadrupole mass spectrometry (QMS) was also utilized to study the Hacac-O_3 etch process on crystalline La_2O_3 powder at 250 °C. $La(acac)_3$ organic fragments were detected during Hacac exposure.During O_3 exposure, combustion products were observed from the oxidation of organic residuals left from Hacac exposures.

Hexafluoroacetylacetone (hfacH) has also been utilized instead of Hacac to etch La_2O_3. One advantage of Hhfac over Hacac is that Hhfac has a lower pKa value and hfac-metal complexes are generally more volatile. However, La_2O_3 ALE using hfacH and O_3 displayed a substantially lower etch rate of 0.06 Å/cycle at 250 °C.This result was attributed to significant film fluorination by Hhfac as revealed by XPS analysis. Etching lanthanum fluoride using the Hhfac-O_3 chemistry is more challenging.

AP-ThP-3 Spontaneous Etching of SiO2 by Co-Adsorbing Polar Molecules with HF, ***Marcel Junige****, Steven M. George,* University of Colorado Boulder

Spontaneous etching is characterized by a physicochemical reaction of a thin film surface with a reactant vapor that releases volatile products with a continuous etch rate. Spontaneous etching provides the benefit of a single processing step with simply one etchant exposure, as well as typically high inherent selectivity.

Previous work has demonstrated that anhydrous HF vapor does not spontaneously etch SiO_2. However, co-adsorbing ammonia (NH_3) with HF has led to rapid SiO_2 spontaneous etching. These results have suggested that the nature of the active etch species changes in the presence of NH_3. Without co-adsorbed NH_3, the active etch species is believed to be F^-. With the polar NH_3 co-adsorbate, the active etch species is thought to switch to HF_2^-. [Junige, George: *Chem. Mater.* **36**, 6950 (2024)]

Co-adsorbing polar molecules with HF has been proposed to form HF_2^- species to enable SiO_2 etching. Examples of suitable polar molecules include dimethylamine ($(CH_3)_2NH$: 1.0 D), NH_3 (1.4 D), methanol (CH_3OH: 1.7 D), water (H_2O: 1.85 D), or ethylene glycol ($(CH_2OH)_2$: 2.28 D); where the number in parentheses refers to the dipole moment of the respective molecule in the gas phase. In theory, these polar co-adsorbates solvate HF and stabilize the dissociation products H^+ and F^-. As a result of this more extensive HF dissociation, F^- species at increased concentration react further with HF to produce HF_2^- species.

In situ spectroscopic ellipsometry (iSE) experiments were performed to test the idea that other polar molecules co-adsorbed with HF may enable SiO_2 spontaneous etching. These investigations revealed that co-adsorbing H_2O or CH_3OH with HF did not spontaneously etch SiO_2 at 200 or 275°C. The adsorption and desorption kinetics of H_2O or CH_3OH molecules at SiO_2 surfaces might not yield an adequate solvation layer at these elevated temperatures. In contrast, co-adsorbing DMA+HF enabled SiO_2 spontaneous etching with a substantial etch rate of 34.70 Å/min at 200°C. Similar results have been observed previously for NH_3+HF co-dosing at 275°C. These results suggested that co-adsorbing polar molecules with HF to form HF_2^- species can etch SiO_2 if there is sufficient solvation. Co-

AP-ThP-6 Atomic Scale Processing (AP7) Sustainable Semiconductor Manufacturing (SM): Oral Session (or Poster)DOE's Sandia Project on Tunnel Field Effect Transistor (TFET) for 10X Microelectronics Energy Efficiency in a General Purpose Transistor*, Desiree Salazar,* CLEAResult Energetics, DOE/AMMTO*; Emilie Lozier,* DOE-EERE*; Shashank Misra,* Sandia National Lab*;* ***Tina Kaarsberg****,* DOE-EERE

Abstract—The United States Department of Energy (DOE) Advanced Materials and Manufacturing Technology Office (AMMTO) is leading a multi-organization effort to counter alarming trends in U.S. computing energy use (e.g. **LBNL 2024 forecasts -** lbnl-2024-united-states-data-center-energy-usage-report.pdf [https://eta-publications.lbl.gov/sites/default/files/2024-12/lbnl-2024-united-states-data-center-energy-usage-report.pdf] - that data centers will account for 26% of US electricity use by 2028 when cyrptomining is included) with its initiative in energy efficiency scaling for two decades (EES2) for microelectronics.Under this initiative, DOE/AMMTO has funded a portfolio of EES2 device technology R&D projects that promise >10X energy efficiency increase by 2030. This [talk] will highlight the first of these projects with Sandia National Laboratories to build on atomically precise manufacturing techniques to create a vertical tunnel field effect transistor (vTFET). Updates will be provided on the successful integration of front end of line (FEOL), back end of line (BEOL) and mid-end of line (MEOL) manufacturing processes (especially thermal budget) to fabricate this vTFET in a CMOS compatible process.One important discovery of the research in this area is "ultradoping" which makes the abrupt doping profiles needed for efficientvTFETs far more manufacturable. This talk also will present how these Sandia results integrate with version 1.0b of the EES2 roadmap that will be issued in Summer 2025. Version 1.0a of the Roadmap is available at EES2 Roadmap Version 1.0 [https://eere-exchange.energy.gov/FileContent.aspx?FileID=f4234e29-cc0c-4a56-a510-86b616ab5535] .

AP-ThP-7 Atomic Layer Deposition of Vanadium Oxide on Silicon Oxide and Kapton Substrates, ***Mohamed Asrif****, Shyam Aravamudhan,* North Carolina A&T State University

Multilayer optical coatings play a vital role in the propagation of light in photonic devices through selective reflection, transmission, and absorption of specific wavelengths. Among transition metal oxides, Vanadium Oxide (VO2) shows significant promise due to its high corrosion resistance at low temperatures, high tensile strength, and high electrical conductivity. This work aims to enhance the performance and durability of optical coatings by depositing VO_2 thin films using Atomic Layer Deposition (ALD), a technique offering precise and conformal deposition of ultra-thin films with Angstrom-level thickness control at low temperatures, making it a preferred method of growing thin films on planar and nanostructured surfaces. Vanadium Oxide (VO2) films were synthesized on Silicon and Kapton Substrates by the ALD method using the precursor Tetrakis (ethylamino) vanadium (TEMAV). Results from XPS confirmed successful deposition, as the binding energies for vanadium (V2p ½ and V2p 3/2 orbitals were both present) and oxygen were both present, as well as residual traces of Carbon and Nitrogen. XRD measurements for the 7 nm sample and the 21 nm sample revealed that the films were amorphous, deposited at 150 °C. AFM results indicated mostly smooth surfaces with an RMS roughness value of between 0.2 and 0.3 nm. However, on a larger scale, that RMS roughness value increased to around 17 nm, indicating that there were signs of agglomeration in the deposition. Raman spectroscopy of the 21 nm sample exhibited spectral features corresponding to mixed oxidation states of vanadium, suggesting partial crystallinity post-annealing. Characterization of the 42 nm samples are still in progress. Post-deposition annealing at ~500 °C in ultra-high vacuum will be utilized to generate crystallization, then samples will undergo comprehensive determination of the structural and surface chemistry.

AP-ThP-8 Development of ALD-ZrN for Diffusion Barrier Layer in ULSI-Cu Interconnects*, Jun Tanaka, Jun Yamaguchi, Noboru Sato, Naoki Tamaoki, Atsuhiro Tsukune,* ***Yukihiro Shimogaki,*** The University of Tokyo, Japan

To achieve higher performance and lower power consumption in ULSI devices, transistors have been continuously miniaturized and integrated at higher densities, resulting in the reduction of Cu interconnect linewidths. However, as the linewidth approaches the mean free path of electrons in Cu (~40 nm), the effects of inelastic electron scattering at grain boundaries and sidewall interfaces become non-negligible, leading to increased resistivity. Furthermore, the conventional diffusion barrier TaN, used to

prevent Cu penetration into interlayer dielectrics, has a much higher resistivity than Cu (Cu:1.68 μΩ·cm, TaN:135 μΩ·cm), and its thickness reduction is limited due to the need to maintain barrier integrity. As a result, the proportion of Cu in the interconnect cross-section decreases with scaling, causing a sharp increase in line resistance. Additionally, increased resistance at the via bottom due to the barrier layer also becomes problematic.

In this study, we focused on ZrN as a novel diffusion barrier material. ZrN possesses the lowest resistivity (13.6 μΩ·cm) among transition metal nitrides [1] and maintains its barrier properties even after annealing at 500 °C [2]. To deposit ZrN films, we employed thermal atomic layer deposition (ALD), which is suitable for conformal coating in narrow damascene trenches. $Zr[N(CH_3)_2]_4$ was used as the precursor, NH_3 as the reactant gas, and N_2 as the carrier/purge gas.

Figure 1 shows the thickness and resistivity of ZrN films deposited at 250 °C as a function of ALD cycles. Film thickness increased linearly with the number of cycles, indicating excellent controllability, although the resulting resistivity was not yet ideal. Figure 2 presents the growth per cycle (GPC) at various deposition temperatures, revealing a stable ALD window between 150 and 250 °C. Figure 3(a) shows the dependence of film density and resistivity on NH_3 supply time for ZrN deposited at 200 °C, which lies within the ALD window. Increasing the NH_3 supply time led to higher film density and lower resistivity. Since no significant change in film composition was observed by XPS (Fig. 3(b)), the densification is attributed to improved surface reactions during the NH_3 pulse. When a film deposited with a 5 sec NH_3 supply was etched using an Ar ion gun in the XPS chamber and its resistance measured, removal of the surface oxide layer significantly reduced the resistance (Fig. 4). Suppressing surface oxidation at elevated temperatures after deposition is expected to further reduce the resistivity.

[1] C. C. Wang *et al.*, *Journal of Materials Science*, **30**, 1627–1641 (1995).

[2] M.B. Takeyama *et a*l., *Japanese Journal of Applied Physics*, **61** SJ0802 (2022).

AP-ThP-9 Comparative Evaluation of SiO2 Atomic Layer Etching Using NF3 and SF6 Gases via a Combined Thermal and Remote Plasma Approach*,* ***Min Kyun Sohn****, Jieun Kim, Sun Kyu Jung, Min-A Park, Jin Ha Kim, Jaeseoung Park, Subin Heo, Sang-Hoon Kim, Jeong Woo Park, Seong Hyun Lee, Dongwoo Suh,* Electronics and Telecommunications Research Institute, Republic of Korea

Atomic Layer Etching (ALE) is a critical technology enabling atomic-scale precision in advanced semiconductor device fabrication. Although obtaining detailed etching characteristics from various fluorine-based gases is crucial for optimizing etch per cycle (EPC) and selectivity, experimental data on gases other than commonly used hydrogen fluoride (HF) or C-F combined gases remain limited. This study investigates silicon dioxide (SiO_2) ALE processes utilizing sulfur hexafluoride (SF_6) and nitrogen trifluoride (NF_3) gases, employing a combined thermal and remote plasma-assisted approach at a process temperature of 300°C. The selection of SF_6 and NF_3 gases was guided by their distinct environmental impacts, radical generation efficiencies, and their potential effects on etching characteristics.

In this study, a surface modification approach using trimethylaluminum (TMA), followed by selective removal with remotely generated fluorine radicals, was systematically evaluated. By combining thermal isotropic surface modification with highly reactive fluorine radicals generated via remote plasma, this method effectively leverages the advantages of both isotropic thermal etching and plasma-enhanced high EPC. Experimental results indicated that NF_3 gas generated significantly higher fluorine radical densities than SF_6 under identical thermal and remote plasma conditions, resulting in enhanced EPC. However, in the case of NF_3 gas flow rates above 20 sccm, the significantly higher density of fluorine radicals generated expanded beyond the ALE regime into conventional plasma etching territory, limiting uniform atomic-level control. In contrast, fluorine radicals generated by SF_6 remained within optimal quantities for true ALE conditions, even at a relatively high flow rate of 100 sccm. Additionally, the remote plasma-assisted method effectively minimized ion-induced surface damage, thus promoting superior etching quality.

Our findings highlight that selecting the appropriate gas (NF_3 or SF_6) based on specific process requirements is critical, as each gas offers distinct advantages. Future research will explore mixed-gas processes combining SF_6 and NF_3 to synergistically enhance their respective benefits and further optimize ALE performance.

AcknowledgmentsThis work was supported by the Electronics and Telecommunications Research Institute(ETRI) grant funded by the Korean government [25ZH1240]

AP-ThP-11 Characterizing Remote Ar/H2 plasmas for Atomic Precision Processing*,* ***David Boris,*** *Maria Sales, Peter Litwin, Michael Johnson, Mackenzie Meyer, Virginia Wheeler, Jeffrey Woodward, Scott Walton,* U.S. Naval Research Laboratory

In comparison to thermal atomic layer deposition (ALD) plasma-enhanced atomic layer deposition (PE-ALD) generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring process conditions to achieve desirable film characteristics. Among the approaches used to tailor film properties is the inclusion of Ar/H2 plasma exposures in the PEALD growth cycle as a means to either mitigate carbon contamination or as a reduction step that converts metal oxide films to metallic films. When employing these Ar/H2 plasma exposures however, control over the flux and energy of ions is needed to avoid unwanted damage to the growth surface. In addition, Ar/H2 plasmas produce atomic H radicals, and VUV photons which also need to be considered when choosing process conditions. In this work we aim to characterize the production of ions, atomic neutrals, and photons within remote Ar/H2 inductively coupled plasma sources commonly used for PEALD. The information gained in characterizing these systems will then be used to guide the choice of process conditions for PEALD growths involving Ar/H2 plasma exposures. Langmuir probe and retarding field energy analyzer (RFEA) measurements were used to characterize the charged particle flux within these systems, and optical emission and VUV emission spectroscopy was used to characterize the atomic H density and VUV photon characteristics respectively. This work is supported by the Office of Naval Research through the Naval Research Laboratory base program.

AP-ThP-12 From Inhibitor to Promoter: Role of Hexafluoroacetylacetone in Tailoring TiO_2 Growth on MgO Surfaces*,* ***Sanuthmi Dunuwila****, John R. Mason, Andrew Teplyakov,* University of Delaware

Magnesium oxide (MgO) is a key material in electronic and optoelectronic devices due to its wide bandgap, optical transparency, and thermal stability. However, the performance of MgO-based multilayer systems is often limited by interfacial inconsistencies, especially when deposited via such techniques as sputtering, which introduce surface defects. Surface modification strategies have emerged to address these issues, particularly in enhancing compatibility with atomic layer deposition (ALD) processes.

This work explores the surface modification of sputter-deposited amorphous MgO films using 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH), a fluorinated β-diketone. Although this compound has been reported as a small-molecule inhibitor in selected ALD processes, this study demonstrates that hfacH acts as a growth promoter for TiO_2 deposition on MgO with thermal ALD that utilizes TDMAT and H_2O as co-reactants. Water contact angle (WCA) measurements confirm that hfacH alters the MgO surface from hydrophilic to hydrophobic, yet TiO_2 nucleation is enhanced on the modified surface, challenging conventional interpretations of surface energy and precursor accessibility.

This study uses a suite of primary surface characterization tools, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray diffraction (XRD), and scanning electron microscopy (SEM) to confirm successful TiO_2 deposition.

These findings challenge the prevailing notion of hfacH as a growth inhibitor and highlight its context-dependent behavior. The modified surface facilitates nucleation, likely due to altered surface energy and local chemical environment, suggesting a potential role for hfacH as a growth promoter. This study contributes to the understanding of molecular surface chemistry and offers new insight into improving interface quality in multilayer oxide systems.

By redefining the function of fluorinated ligands in ALD chemistry, this work opens opportunities for more controlled and efficient deposition strategies in advanced electronic device fabrication.

AP-ThP-13 Chemistry of a 2D Material Fe_3GaTe_2 for Atomically-Precise Processing: Etching and ALD*,* ***Marissa D. Piña****, Andrew V. Teplyakov,* University of Delaware

Fe_3GaTe_2 is a 2D van der Waals material that displays intrinsic ferromagnetism above room temperature along with strong perpendicular anisotropy, making it a possible candidate for spintronics and magnonics applications. Recent computational studies have shown that the Fe_3GaTe_2 Curie temperature becomes elevated and its magnetic properties are

tunable at the monolayer, demonstrating the importance of obtaining ordered and defect-free thin film and monolayer structures of this material by using atomically-precise treatments.

To determine whether Fe_3GaTe_2 can be etched controllably in nearly atomic layer etching regime, we performed a chlorine gas dose followed by an acetylacetone dose on Fe_3GaTe_2 flakes exfoliated onto a silicon substrate. AFM and XPS after the chlorine dose at elevated temperature show a partially etched but rougher surface. The consequent acetylacetone dose at the same temperature shows further etching. We aim at exploring atomic layer etching of Fe_3GaTe_2 under further optimized and controlled conditions. We are also exploring the etching mechanism to determine why the chlorine dose causes the initial change.

To explore the role of surface structure and chemistry of Fe_3GaTe_2 in ALD reactivity and also to determine whether ALD is feasible on Fe_3GaTe_2 flakes, we followed the ALD of Al_2O_3 on unmodified Fe_3GaTe_2 flakes. We observed alumina growth from TMA/water deposition cycles on Fe_3GaTe_2 after 10 and 30 cycles in a similar amount compared to what was grown on the reactive silicon substrate, as confirmed by ToF-SIMS depth profiling. We are currently evaluating the changes in Al_2O_3 growth after chemical surface modification of Fe_3GaTe_2 with small organic molecules.

AP-ThP-14 Atomic Layer Etching of HfO_2 and ZrO_2 on Nanotrench Structures Using NbF_5 and $TiCl_4$*, Boyun Choi*, *Getasew Zewdie, Hyeyoung Shin, Nari Jeon,* Chungnam National University, Republic of Korea

High-k oxides such as HfO_2 and ZrO_2 are critical for advanced transistor integration, but their atomic-level patterning remains a bottleneck. We examined thermal atomic layer etching (ALE) of these oxides using NbF_5 and $TiCl_4$. Distinct material-dependent behaviors were observed: HfO_2 exhibited smooth, self-limiting etch per cycle, whereas ZrO_2 showed significant surface roughening and high Cl incorporation. Surface chemical analysis confirmed that the degradation in ZrO_2 arises from unstable chlorinated intermediates. Density functional theory (DFT) calculations support this interpretation, indicating stronger and more disruptive $TiCl_4$ interactions with ZrO_2 compared to HfO_2. ALE was further applied to nanohole structures with 150 nm diameter and 2000 nm depth. In this geometry, HfO_2 displayed topographically selective removal, attributed to crystallinity-related microstructural variations across the etched regions. These results demonstrate that both reactant chemistry and oxide microstructure govern ALE performance. The combined experimental and computational insights provide a framework for selective patterning of high-k dielectrics and offer process guidelines for enabling integration of HfO_2 and ZrO_2 in future nanoscale transistor and interconnect architectures.

AP-ThP-16 Area-Selective Deposition with Aromatic Self-Assembled Monolayer Blocking Layers*, Michelle Paquette*, *Andrew Molder, Raja Bale,* University of Missouri-Kansas City*; Sharmistha Bhattacharjee, Ben Garland,* Lehigh University*; Nathan Oyler,* University of Missouri-Kansas City*; Nicholas Strandwitz, Vamseedhara Vemuri,* Lehigh University

Area-selective deposition (ASD) is an important strategy in improving the fidelity of and/or reducing the complexity of current semiconductor patterning processes. Dielectric on dielectric (DoD) deposition is of interest for fully self-aligned via flow; however known DoD processes are limited in terms of materials, selectivities, and processing ranges. A common strategy for achieving ASD is to use a blocking layer on the non-growth surface (e.g., a metal) to be able to deposit a target material selectively on the desired surface (e.g., a dielectric). The most well-established blocking layers are self-assembled monolayers (SAMs) based on long alkyl chains, such as dodecanethiol. While these have demonstrated extremely promising results, they present limitations such as restricted processing windows (e.g., temperature), a typical requirement for solution-phase processing, long exposure times, limited stability (temperature, time, chemical), and presence of defects (e.g., pinholes) resulting from disorder or alkyl chain distortions. We have investigated an alternative class of blocking layers based on aromatic thiol SAMs, sometimes referred to as small molecule inhibitors. We demonstrate how the atomic structure of the aromatic derivative influences SAM formation and blocking ability, and demonstrate improved blocking of typical atomic layer deposition oxide films over state-of-the-art dodecanethiol SAMs.

AP-ThP-17 Thermal Characterization of Carborane Compounds for Advanced Thin Film Deposition*, Michael Stoll*, *Gynendra Bhattarai, Rupak Thapa,* University of Missouri-Kansas City*; Mark Lee,* Twelfth Vertex LLC*; Nathan Oyler, Michelle Paquette,* University of Missouri-Kansas City

Carboranes, with their unique icosahedral boron-based cage structures, are promising molecular precursors for advanced thin film deposition techniques such as plasma-enhanced chemical vapor deposition (PECVD) and molecular layer deposition (MLD). Their high vapor pressures and chemical stability make them ideal for vapor-phase delivery in high- and ultra-high vacuum systems, enabling the fabrication of ultra-pure films. We report the following thermal properties of a series of carborane compounds: vapor pressure, enthalpy of sublimation, melting points, and specific heat capacities. Using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), optimized isothermal and dynamic measurement protocols were developed with benzoic acid as a calibration standard to ensure precision. Vapor pressure curves were constructed, and Antoine coefficients were derived to characterize the compounds over a temperature range suitable for deposition (0.1–10 Torr at <200 °C). The results provide critical insights into the vapor pressures, thermal stability and phase behavior of carboranes, advancing their application in next-generation electronic devices and novel material architectures.

Authors: MS Michael Stoll, PhD Gyanendra Bhattarai, PhD Rupak Thapa, PhD Mark Lee, PhD Nathan Oyler, PhD Michelle Paquette

AP-ThP-18 Atomic Layer Deposition of Iridium from (EtCp)Ir(CHD) and Molecular Oxygen on the Anric AT650P ALD Tool*, Eliza Spear,* Anric Technologies*; Mughees Khan,* Harvard University Center for Nanoscale Systems*; Philippe de Rouffignac,* Anric Technologies

Iridium metal films were deposited by atomic layer deposition (ALD) reaction between 1-ethylcyclopentadienyl-1,3-cyclohexadieneiridium(I) [(EtCp)Ir(CHD)] and molecular oxygen at 250 °C in the Anric AT650P ALD tool. The Ir growth rate was 0.5 Å/cycle. Ir films were growth on thermally oxidized SiO_2 with and without a 10 nm Ta_2O_5 interlayer. Ir films grown on Ta_2O_5 appear smoother and more continuous under SEM compared to films on SiO_2, consistent with a previous report by Schmitt et al. for Ir grown from ALD with $Ir(acac)_3$ and oxygen, who report that Ta_2O_5 delays Ir nucleation and yields higher substrate coverage compared to SiO_2 [1]. The resistivity of a 42 nm Ir film on Ta_2O_5 was ca. 12 µΩ-cm. Optical properties of iridium films were modeled using variable angle spectroscopic ellipsometry with interference enhancement [2]. An extinction coefficient >5 at 633 nm was obtained for Ir films thicker than 20 nm on Ta_2O_5.

[1] P. Schmitt et al. Coatings 2021, 11, 173. DOI: 10.3390/coatings11020173

[2] J. N. Hilfiker et al. Thin Solid Films 2008, 516, 7979-7989. DOI: 10.1016/j.tsf.2008.04.060

AP-ThP-19 Plasma-enhanced Atomic Layer Etching of Tungsten Disulfide*, Jeremy Mettler*, *Justin Boles, Vincent Donnelly,* University of Houston

Transition-metal dichalcogenides (TMDs) are a class of 2D materials of interest for future semiconductor devices due to their favorable scaling properties compared to bulk 3D materials. These materials take the general form of MX_2, where M is a transition metal such as Mo or W and X is a chalcogen such as S or Se. TMDs are inherently 2D, consisting of in-plane covalently bonded sheets held together by cross-plane van der Waals forces which render the “bulk” monolayer surface-terminated. While these materials hold promise in semiconductor applications, processes for high-volume manufacturing of TMDs remain in the early stages of development. One key challenge is obtaining uniform, monolayer growth of TMD films over large areas, which is currently challenging using CVD growth which often results in the formation of multilayer “islands”. Controllable subtractive processes such as atomic layer etching (ALE) may be useful in etching back these features, yielding large area monolayer films. While some TMDs such as MoS_2 have been more thoroughly studied, other promising materials such as WS_2 require further study to develop at-scale processes for ALE. To achieve ALE of WS_2 in this work, a two-step process was employed. First, films of WS_2 were exposed to fluxes of oxygen radicals in the afterglow of an Ar/O_2 inductively coupled plasma (ICP). In the absence of ion bombardment oxygen radicals removed S from the surface and formed a tungsten oxide layer 1-2 monolayers thick (as measured using in-situ XPS). Next, an Ar/BCl_3 plasma was used to selectively etch the tungsten oxide layer relative to the underlying WS_2. While no etching was observed in the afterglow, direct exposure to the ICP plasma without substrate bias was able to significantly reduce the tungsten oxide concentration after 10s, with complete removal occurring after ~40s. XPS measurements following the BCl_3 process confirmed the WS_2 film was restored to pre-processing stoichiometry and that the etch process was

self-limited to 1-2 monolayers/cycle. Optical emission spectroscopy was used to monitor etchant species, and the BCl_3 was observed to be highly dissociated, primarily forming BCl rather than BCl_2.

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