Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+PS+TF-MoM

Thermal Atomic Layer Etching and Deposition

Moderator: Jean-Francois de Marneffe, IMEC, Belgium

8:20am **AP+PS+TF-MoM-1 Atomic Layer Etching of Aluminum and Aluminum Oxide for Optical Applications**, ***John Hennessy***, *R. Rodríguez, A. Jewell,* Jet Propulsion Laboratory **INVITED**

Thermal atomic layer etching can be utilized for the surface preparation of aluminum in order to improve its optical performance at ultraviolet wavelengths. In this work we report on the use of trimethyaluminum and anhydrous hydrogen flyoride to remove the native oxide of aluminum prior to encapsulation with fluoride dielectric materials. This ALE/ALD process is used for the fabrication of reflective coatings and bandpass filters operating at wavelengths shorter than 200 nm. The etch rate of aluminum oxide is observed to be dependent on chamber conditioning with a significant enhancement in etch rate observed when the cyclic etching is performed in the presence of alkali halide materials. This enhancement can reduce the temperature threshold where etching dominates the reaction cycle over deposition.

The reduction of the overall processing temperature can enhance the compatibility of the full coating process with some temperature-sensitive substrates, and limit the amount of etch damage experienced by aluminum surfaces. Etching into the aluminum surface is generally observed to result in non-conformal etching which greatly increases the surface roughness of films and degrades the optical performance of resulting structures. Reducing the etch temperature can mitigate this effect by increasing the selectivity of the native oxide removal over the underlying metal. Optimization of these processes may provide insight into achieving conformal ALE of aluminum surfaces. The extension of these atomic layer processing methods towards the fabrication of meter-class mirror coatings is also discussed in the context of future large UV space observatories for NASA astrophysics applications.

9:00am **AP+PS+TF-MoM-3 Thermal Etching of First Row Transition Metal Oxides using Acetylacetone and O_3: Pathway for Atomic Layer Etching**, ***Jonathan Partridge***[1], *S. George,* University of Colorado at Boulder

Etching metal oxides with halogen-free methods is important during processing to avoid corrosion.Acetylacetone (Hacac) is an organic hydrocarbon.Hacac can supply acac ligands that can form volatile metal complexes with most transition metals.Consequently, Hacac can spontaneously etch metal oxides to form $M(acac)_x$ and H_2O.One difficulty is that Hacac can also decompose on the metal oxide surface and block the spontaneous etching.However, this surface poisoning also leads to a self-limiting reaction. The O_3 exposure can then remove the carbonaceous decomposition species and produce a pathway for atomic layer etching.

Thermal etching of first row metal oxides was demonstrated using Hacac and O_3 at pressures of 2.5 Torr at 250 °C.A quadrupole mass spectrometer (QMS) reactor with molecular beam expansion and line-of-sight to the ionizer was employed to detect etch species with high sensitivity.Metal oxide nanopowders were used to maximize the surface area and signal intensity of the etch products. The reactant sequence used five sequential Hacac exposures, one O_3 exposure, and one final Hacac exposure to check for etch product enhancement after O_3 exposure.Etching was monitored by the production of $M(acac)_x$ etch products.

$M(acac)_x$ etch products were observed for Sc_2O_3, V_2O_5 and VO_2, Cr_2O_3, Mn_2O_3 and MnO, Fe_2O_3 and Fe_3O_4, Co_3O_4 and CoO, CuO and Cu_2O, and ZnO. No etching was observed for TiO_2, MnO_2, and NiO. The metal oxides that etched either displayed (1) spontaneous etching by Hacac with no self-limiting behavior or (2) etching that limited itself versus Hacac exposure.The metal oxides that were spontaneously etched by Hacac were Mn_2O_3 and MnO, Co_3O_4 and CoO, and ZnO.The metal oxides that displayed self-limiting behavior were Sc_2O_3, V_2O_5 and VO_2, Cr_2O_3, Fe_2O_3 and Fe_3O_4, and CuO and Cu_2O.ALE processes for these metal oxides that displayed self-limiting reactions are possible using Hacac and O_3.

A comparison between the $M(acac)_x$ etch products and the metal oxide also provided information about oxidation state changes during etching.The x in $M(acac)_x$ is both the number of acac ligands and the oxidation state of the M metal center.Sc_2O_3, Cr_2O_3, MnO, Fe_2O_3, CoO, CuO, and ZnO all formed $M(acac)_x$ etch products with the same oxidation state as the metal oxide.In contrast, the other metal oxides all displayed evidence for reduction during etching.This reduction may occur by oxygen loss during the combustion of Hacac.

9:20am **AP+PS+TF-MoM-4 Selectivity between Silicon-Based Materials for Thermal Atomic Layer Etching and Spontaneous Etching**, ***Marcel Junige***, *S. George,* University of Colorado at Boulder

Sub-10-nm technology nodes must overcome the limits of photolithography. This requires selectivity between various Si-based materials for thermal atomic layer etching (ALE) and spontaneous etching. This work examined selectivity between silicon dioxide (SiO_2) and silicon nitride (SiN_x) for thermal ALE using trimethylaluminum (TMA) and hydrogen fluoride (HF), as well as for spontaneous etching using HF alone, at 275℃. Distinct etch rates between SiO_2 and SiN_x achieved inherent selectivity.

Experiments were conducted in a hot-wall, viscous-flow vacuum reactor with good control over the pressure during static reactant dosing to ensure reproducibility. *In situ* spectroscopic ellipsometry (iSE) was utilized to study etch-per-cycle (EPC), synergy, and selectivity characteristics. Sodium bifluoride ($NaHF_2$) was tested as an alternative HF source. $NaHF_2$ is a solid salt with negligible HF vapor pressure at room temperature, making $NaHF_2$ safer to handle than HF-pyridine. $NaHF_2$ delivered HF pressures up to 15 Torr when heated to 150℃ without releasing sodium. During thermal ALE of alumina (Al_2O_3), $NaHF_2$ exhibited diffusion-limited fluorination and EPC characteristics comparable with HF-pyridine.

For thermal ALE of SiO_2 alternating TMA and HF, the EPC and synergy were –0.2 Å and 88%, indicating minor spontaneous etching by HF alone. This moderate synergy for SiO_2 thermal ALE improved to 95% by ensuring water-free conditions during fluorination. On the other hand, the EPC for SiN_x thermal ALE was –1.1 Å. The EPC for SiN_x was expected to be much lower than for SiO_2 because no oxygen reactant was employed to oxidize SiN_x. However, iSE experiments revealed that repeated exposures of HF alone spontaneously etched SiN_x. Anhydrous HF vapor might form F^- species at the surface that have been attributed to dominate SiN_x etching. Spontaneous etching using static exposures of 45 s at 3 Torr HF alone obtained a high selectivity of ~50:1 for SiN_x removal over SiO_2 retention.

For thermal ALE alternating TMA and HF in co-dose with ammonia (NH_3), the selectivity inverted to ~9,000:1 for SiO_2 over SiN_x. HF+NH_3 co-dosing led to rapid spontaneous etching of SiO_2. NH_3, similar to water, might facilitate the dissociation of HF into H^+ and F^-, where the increased F^- concentration immediately produces HF_2^- species. HF_2^- species have been attributed to dominate SiO_2 etching.

In conclusion, this work demonstrated conditions for inherently selective gas-phase etching of either SiO_2 or SiN_x.

9:40am **AP+PS+TF-MoM-5 Thermal Atomic Layer Etching of SnO_2 by Fluorination and Ligand-Exchange Using HF and $Al(CH_3)_3$**, *C. Li,* University of Colorado Boulder, China*; J. Partridge,* ***Steven George,*** University of Colorado Boulder

Thermal atomic layer etching (ALE) can be achieved with sequential, self-limiting surface reactions. One mechanism for thermal ALE is based on fluorination and ligand-exchange reactions. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming volatile products. Previous studies have successfully applied this thermal ALE strategy for Al_2O_3, HfO_2, and ZrO_2 ALE. However, no previous investigations have explored the thermal ALE of SnO_2 films.

This study demonstrated the thermal ALE of SnO_2 thin films using sequential, self-limiting thermal reactions with hydrogen fluoride (HF) and trimethylaluminum ($Al(CH_3)_3$, TMA) as the reactants. The initial SnO_2 films were grown by atomic layer deposition (ALD) using tetrakis(dimethylamino) tin and H_2O_2. The thermal SnO_2 ALE process was then studied using various techniques including quartz crystal microbalance (QCM), spectroscopic ellipsometry (SE), and quadrupole mass spectrometry (QMS).

In situ QCM experiments monitored SnO_2 ALE at temperatures from 250 to 300 ℃. The SnO_2 etching was linear versus the number of HF and TMA reaction cycles. The QCM studies also showed that the sequential HF and TMA reactions were self-limiting versus reactant exposures. The SnO_2 etching rates increased at higher temperatures. The QCM analysis measured mass change per cycle (MCPC) values that varied from −44.32 ng/(cm^2 cycle) at 250 °C to −123.5 ng/(cm^2 cycle) at 300 °C. These MCPCs correspond to SnO_2 etch rates from 0.64 Å/cycle at 250 °C to 1.78 Å/cycle at 300 °C.

SE measurements confirmed the linear removal of SnO_2 and the etching rates. QMS analysis also revealed the volatile etching products during the

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

sequential HF and TMA exposures on SnO_2 at 300 °C. These QMS investigations observed $Sn(CH_3)_3^+$, indicating $Sn(CH_3)_4$ as the etch product during TMA exposures. $Al_xF_y(CH_3)_z$ dimer and trimer species were identified as the ligand-exchange products. QMS analysis during multiple sequential TMA doses before HF/TMA cycling also revealed that fluorination was necessary for $Sn(CH_3)_4$ etch product evolution. This observation indicated that TMA does not convert SnO_2 to Al_2O_3. The results indicate that thermal SnO_2 ALE using sequential HF and TMA exposures occurs by fluorination and ligand-exchange reactions.

10:40am **AP+PS+TF-MoM-8 Reactivity and Volatility as Key Metrics for Classifying the Substrate Selectivity of Ligands in Atomic Level Processing***,* ***Hadi Abroshan,*** Schrödinger, Inc.*; S. Lim,* Schrödinger, Inc., Republic of Korea*; A. Chandrasekaran,* Schrödinger, Inc.*; S. Elliott,* Schrödinger, Inc., Germany*; H. Kwak, M. Halls,* Schrödinger, Inc.

One of the main challenges in the area-selective deposition or etch for semiconductor processing is finding a single reagent that undergoes different chemistry on different substrates. The reagent may be an organometallic complex containing a particular ligand or may be the protonated version of that ligand. In this work we propose that examining just two properties of the organometallic complex across a series of metal cations is sufficient to give an indication of the area-selectivity that can be achieved with reagents based on the particular ligand chemistry.

The first property is reactivity towards the hydrolysis reaction, which gives information about oxide formation versus surface passivation or etching, and the second property is volatility of the organometallic reagent or etch by-product. Figure 1a shows the four limiting cases of the combination of these two properties. Using quantum chemical and machine learning methods to predict the properties, such reactivity-volatility maps can be plotted quickly for a wide range of ligands and metal-containing substrates. We validate our results on the chloro ligand (Figure 1b), thd, RCp and NR2 against area-selective experiments, including those using HCl as etchant [1], ruthenocene and ferrocene [2] as metal sources and β-diketonates as inhibitors [3]. While approximate, this approach provides a starting point for designing and understanding atomic-level processes that are area-selective with respect to a wide variety of substrates.

[1] M.F.J. Vos et al., Chem. Mater. 31, 3878 (2019).

[2] H. Nadhom et al., J. Phys. Chem. Lett. 12, 4130 (2021).

[3] A. Mameli et al., ACS Nano 11, 9303 (2017).

11:00am **AP+PS+TF-MoM-9 Etching of Silicon Nitride Using Vapor-Phase HF Exposures at Various Temperatures: Role of Ammonium Hexafluorosilicate Salt***,* ***Vahid Ghodsi,*** *S. George,* University of Colorado Boulder

The etching of silicon nitride (SiN_x) was explored using vapor-phase HF exposures at various temperatures. The investigations were performed using *in situ* quadrupole mass spectrometry (QMS) and *ex situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to detect the volatile and non-volatile etch products, respectively. These QMS and ATR-FTIR studies provide valuable understanding of the SiN_x atomic layer etching (ALE) process employing hydrofluorocarbon plasma to form $(NH_4)_2SiF_6$ salt at low temperatures and then thermal annealing at higher temperatures to desorb the salt [N. Miyoshi *et al.*, Jpn. J. Appl. Phys. **56,** 06HB01 (2017)].

At low temperatures, T≤60°C, QMS detected the evolution of SiF_4 from HF exposure at 0.5 Torr on SiN_x. SiF_4 formed concurrently with the formation of a $(NH_4)_2SiF_6$ salt layer on the SiN_x surface according to: $Si_3N_4 + 16HF(g) \longrightarrow 2(NH_4)_2SiF_6 + SiF_4(g)$. To verify the presence of the salt, the temperature could be ramped up to 200°C in the absence of HF exposure. During this temperature ramp, QMS detected SiF_4 at higher temperatures T≥80°C corresponding to the thermal decomposition of the $(NH_4)_2SiF_6$ salt according to: $(NH_4)_2SiF_6 \longrightarrow 2NH_3(g) + 2HF(g) + SiF_4(g)$.

When the HF exposure was performed at higher temperatures T≥120°C, SiF_4 was again observed as an etch product. However, no secondary rise of SiF_4 was detected by QMS during the temperature ramp to 200°C in the absence of HF exposure. This behavior indicated that the $(NH_4)_2SiF_6$ salt did not form on the surface at temperatures T≥120°C. The spontaneous etching of SiN_x with no salt on the SiN_x surface is possible at these higher temperatures. ATR-FTIR studies corroborated the salt formation at lower temperatures and the salt decomposition at higher temperatures.

To demonstrate that HF exposures could achieve high SiN_x etch rates without salt formation, experiments were conducted at T≥140°C with higher HF pressures. A four-fold increase in HF pressure to 2.0 Torr led to a ~five-fold increase in SiF_4 signal intensity measured by QMS. At these higher temperatures T≥140°C, SiN_x etching can proceed with no inhibition from the salt.

11:20am **AP+PS+TF-MoM-10 Crystal Phase Transformations During Thermal Atomic Layer Etching of Hafnium–Zirconium Oxide (HZO) Using Hydrogen Fluoride and Dimethylaluminum Chloride***,* ***Aziz Abdulagatov,*** *J. Partridge,* University of Colorado at Boulder*; M. Surman,* ASM Microchemistry Ltd., Finland*; S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) was previously demonstrated using hydrogen fluoride (HF) and dimethylaluminum chloride (DMAC) [1]. This current work focused on crystallographic transformations of HZO during ALE. Grazing incidence x-ray diffraction (GIXRD) analysis of initial 10 nm thick HZO film on 20 nm thick TiN on Si revealed orthorhombic (o-phase), tetragonal (t-phase), and monoclinic phases (m-phase). *Ex situ* spectroscopic ellipsometry and X-ray reflectivity (XRR) measurements showed that sequential exposures of HF and DMAC at 250 °C resulted in a linear decrease in film thickness with an HZO etch rate of ~0.45 Å/cycle.

GIXRD studies observed that the peaks associated with the o- and t-phases decreased faster in intensity than the m-phase peaks. As the number of ALE cycles increased, only the m-phase remained before the majority of the HZO film was removed by etching. Interestingly, as o- and t-phases were removed, the grain size of the m-phase crystallites increased in size according to the Scherrer equation. XRR investigations also monitored a decrease in the film density with ALE. In addition, atomic force microscopy (AFM) measurements observed that the density decrease was accompanied by an increase in film roughness.

Powder diffraction (PXRD) studies were also conducted to investigate the phase transformation of crystalline ZrO_2 powder at 250 °C. ZrO_2 powder was used as a model system since the chemical properties of HfO_2 and ZrO_2 are very similar. PXRD analysis of as-received ZrO_2 powder showed crystallographic planes of mostly m-phase with some cubic (c-phase) and t-phase. As expected, the etching of ZrO_2 powder resulted in a mass loss. PXRD also observed the loss of c- and t-phases and an increase in grain size of m-phase crystallites. The results for the HZO films and ZrO_2 powder are similar. There are crystal phase transformations that occur with loss of o- and t-phases and growth of m-phase during thermal ALE.

[1] J. A. Murdzek and S. M. George, J. Vac. Sci. Technol. A 38, 022608 (2020)

11:40am **AP+PS+TF-MoM-11 Novel Conversion Half-Cycle for Thermal ALD of High-Density Hfo_2 and Its Use in HfO_2/Al_2O_3 Nanolaminate Dielectric Barriers***,* ***Dane Lindblad,*** Forge Nano

Hafnium dioxide, HfO_2, is an attractive material for use as a dielectric barrier in high-power SiC and GaN electronics, both MOSFET and HEMT, due to its high dielectric constant and thermal stability. Current techniques for depositing HfO_2 by thermal atomic layer deposition (ALD) tend to produce low density and performing films. While plasma enhanced ALD (PEALD) is employed to improve the performance, the high field and fast switching requirements of the device can make the barriers insufficient. In addition, not all applications can accommodate plasma. As such, a novel conversion process, referred to as the “CRISP” process, for the deposition of HfO_2 via thermal ALD has been explored. Utilizing the tool’s unique ability to introduce a small amount of non-metal catalyst during the conversion half-cycle, the CRISP process employs surface catalysis to increase growth per cycle, improve stoichiometry, increase density, and modify crystal morphology compared to HfO_2 films grown with conventional conversion methods, O_3, as shown in Figure 1 and Table 1 below. A comparison of the HfO_2 films grown using the CRISP process and the conventional O_3 process, both deposited at 250°C, will be presented. Furthermore, due to the layer-by-layer growth of ALD, this deposition technique lends itself well to the fabrication of nanolaminate materials. Specifically, HfO_2/Al_2O_3 laminate stacks can be precisely manufactured to alter the bulk material properties and curate device performance, allowing one to choose improvements in leakage current or dielectric breakdown in the nanolaminate film. An initial investigation into the performance of various HfO_2/Al_2O_3 laminate stacks is presented, and this work, coupled with higher quality HfO_2 films, gives insight into the use of these materials for the next generation of high-power electronic devices.

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+PS-MoA

Plasma Enhanced Atomic Layer Etching

Moderators: Robert Bruce, IBM Research, T. J. Watson Research Center, **Scott Walton**, Naval Research Laboratory

1:40pm **AP+PS-MoA-1 Chemical Contrast by Nitridation for Improving Atomic Layer Etching Selectivity in Interconnect and EUV Absorber Applications***, **Taylor G. Smith**[1],* University of California, Los Angeles*; J. de Marneffe, V. Philipsen,* IMEC, Belgium*; J. Chang,* University of California, Los Angeles

As extreme ultraviolet lithography (EUVL) dominates the fabrication of future integrated circuits, advanced EUV photomask absorber materials such as Ni and Ni-Al alloys are needed. As Ru emerges as the capping layer for EUV absorber and a potential supplementary material for backend interconnects, the fact that Ru etches rapidly in oxygen requires a different approach (e.g., nitridation) to create the needed chemical contrast for atomic layer etching. In this work, we present a plasma-thermal atomic layer etching (ALE) approach to etch Ni that relies on nitriding the metal surface using nitrogen plasma, then removing the surface metal nitride with formic acid (FA) vapor. Previous work relied on oxygen plasma as the modification step to form a surface NiO [1]. However, oxygen plasma is known to etch Ru, the standard capping material in EUVL masks. Here we explore a nitrogen plasma-based ALE process to increase the selectivity of the Ni etch to the Ru capping layer. An additional motivation for exploring nitridation-based ALE is that metal nitrides, unlike metal oxides, do not form spontaneously in air, making it possible to ascertain that all surface metal nitride formation must be a result of the plasma processing.

The composition of the metal nitride layer is measured by X-ray photoelectron spectroscopy (XPS) and is controlled by varying the plasma power, pressure, and exposure time. Ni films nitridized in a 500 W, 35 mTorr nitrogen plasma for 5 min have a surface composition of $Ni_{2.8}N$, close to the stoichiometric Ni_3N composition. XPS also confirmed the removal of the surface Ni_xN after exposure to FA vapor at 80°C as manifested by the disappearance of the metal nitride N 1s peak at 397.6 eV. The thickness of the Ni films as a function of ALE cycles is measured by scanning electron microscopy (SEM) and spectroscopic ellipsometry (SE), with the etch rate measured by SE being 0.49 ± 0.20 nm/cycle. We also determine the selectivity of the plasma nitridation ALE process to common hardmasks and to Ru. Finally, we extend this plasma nitridation ALE chemistry to Ni-Al alloys, determining both the etch rate and the stoichiometry changes in the film as a function of ALE cycles.

1. X. Sang and J. P. Chang, J. Vac. Sci. Technol. A **38** (4), 042603 (2020).

2:00pm **AP+PS-MoA-2 Anisotropic and Selective Atomic Layer Etching of Ruthenium***, **Owen Watkins**,* University of California at Los Angeles*; H. Simka,* Samsung*; J. Chang,* University of California at Los Angeles

Ruthenium has been proposed as a replacement for copper in sub-10 nm interconnects, where it has a lower resistivity and does not need as thick of a diffusion or adhesion layer. Ruthenium is known to be etched aggressively in an oxygen plasma by the formation of RuO_4. A reactive ion etching process using plasma with both O_2 and Cl_2 is a direct, high etch rate method, but there is a need to achieve better control and selectivity in order for Ru to be a viable interconnect material. In this work, a thermodynamic approach was first taken to determine viable chemistries. It confirmed that Ru and RuO_2 react with atomic O spontaneously to form RuO_4, and with atomic N to form a metastable RuN layer.RuN reacts with atomic O, but the reaction is less favorable, and can be reduced by H and H_2 into metallic Ru. The thermodynamic assessment led to a novel three-step process to control the etching of ruthenium where a nitrogen plasma forms RuN on the surface of the ruthenium thin film, a hydrogen plasma reduces some of the RuN, creating a surface layer of Ru, then an oxygen plasma etches this topmost layer of Ru but is unable to etch into the RuN.Experimental validation was first realized by exposing blanket Ru film to the sequential process. Compared to a baseline of continuous O_2 plasma with equal conditions and total exposure time as the O_2 plasma step, the three-step process shows an increase in RMS surface roughness of 0.05 nm/cycle and a post-etching resistivity of 30 μΩ-cm, whereas continuous O_2 plasma shows an increase of 0.2 nm/30s of exposure and a post-etching resistivity of 280 μΩ-cm.

Finally, using a SiO_2-patterned Ru structure, a highly anisotropic etch profile was obtained:the nitrogen plasma exposure forms RuN on the exposed surface and sidewalls. Hydrogen plasma with an applied bias anisotropically reduces RuN. Then, an oxygen plasma selectively etches Ru while leaving RuN on the sidewall intact. By creating the anisotropy in the previous steps, a gentler O_2 plasma exposure can be used, which results in anetch rate of 4 nm per cycle and a selectivity of Ru vs. SiO_2/Si_3N_4 of 15, compared to conventional O_2 + Cl_2 RIE plasma etching in literature that reports etch rates in excess of 40 nm per minutes and selectivities around 6.

2:20pm **AP+PS-MoA-3 Mechanisms and Benefits of Cryogenic Processes in Silicon Based Material Atomic Layer Etching***, **Remi Dussart**, R. Ettouri, J. Nos, G. Antoun, P. Lefaucheux, T. Tillocher,* GREMI CNRS/Université d'Orléans, France **INVITED**

Since its introduction in 1988, plasma cryogenic processing has been applied to deep etching of silicon for microelectronics and MEMS devices. High aspect ratio structures can be obtained at very low temperature (typically -100°C) of the substrate in SF_6/O_2 plasma. The mechanism is based on a passivation SiO_xF_y layer, which forms at low temperature only. The formation of this passivation layer has been characterized by in-situ diagnostics such as ellipsometry, mass spectrometry and XPS. SiF_4 molecules which correspond to the main by products of silicon etching by fluorine can also participate in the passivation layer formation and reinforce it. The composition of the SiO_xF_y layer formed in SiF_4/O_2 plasma strongly depends on temperature. In particular, the fluorine content significantly increases below a temperature threshold between -60°C and -100°C. However, this threshold is reached at higher temperature if we process a Si_3N_4 surface instead of a Si surface.

We can take advantage from these interesting properties at cryogenic temperature to develop new cryo-ALE processes. In this presentation, two different types of cryo-ALE will be introduced. The first one is based on the physisorption of C_4F_8 molecules without plasma followed by an argon plasma step to etch SiO_2 at the atomic scale. The second one consists in alternating SiF_4/O_2 plasma interacting with a cooled substrate with argon plasma. During the SiF_4/O_2 plasma, the passivation layer composition can be tuned depending on temperature and substrate material surface. In particular, we will show that a very good etch selectivity between Si_3N_4 and Si can be obtained at a temperature of -65°C for which a very low etch rate is obtained for Si while Si_3N_4 surface is etched at a higher rate. This property can be explained by the chemical analysis of the two surfaces at low temperature. Finally, some experiments of cryoetching in CHF_3/Ar plasma will be presented showing some interesting trends at low temperature on different silicon based materials.

3:00pm **AP+PS-MoA-5 Damage Formation Analyses of Steady Plasma-Enhanced Atomic Layer Etching for Silicon Nitride with Molecular Dynamics Simulations***, **Jomar U. Tercero**[2],* Osaka University, Japan*; A. Hirata,* Sony Semiconductor Solutions Corporation, Japan*; M. Isobe, K. Karahashi,* Osaka University, Japan*; M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; S. Hamaguchi,* Osaka University, Japan

Molecular dynamics (MD) simulations were performed to study the etching mechanisms and surface damage formations during the plasma-enhanced atomic layer etching (PEALE) of silicon nitride (SiN). PEALE is a thin-layer etching technique to achieve a uniform and precisely etched material surface. The typical ALE process consists of alternating self-limiting adsorption and desorption steps. In the adsorption step, the material is exposed to reactive species, which modifies the surface layer. In contrast, in the desorption step, the modified surface is bombarded with low-energy inert ions, resulting in the removal of the modified layer. A recent report on SiN PEALE processes with hydrofluorocarbon (HFC) radical adsorption and Ar ion impacts has shown that C tends to accumulate on the surface, which causes an etch stop [1]. Our simulations of an ideal PE-ALE system with CH_2F radical adsorption and Ar ion bombardment have revealed that the remaining C atoms from the initial ALE cycle can trigger the C accumulation. The surface damage was also observed due to the ion bombardment. Due to the formation of a C layer, high-density Si-C bonds were found to remain on the surface after several ALE cycles, causing further accumulation of C atoms. Therefore, we introduced a short O_2 plasma irradiation process after the desorption step to help remove the problematic C atoms [2]. Our simulations agree with the experimental observations that the additional O_2 plasma irradiation step can prevent the etching from stopping. The Si-C bonds were minimized since O atoms reacted with the C atoms, forming CO

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

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

and CO_2 species. Regardless, Ar ions with sufficient incident energy are still needed for the etching to proceed, which can cause damage to the etched surface. To understand the effect of the energetic ions in the desorption step, we also performed SiN PEALE with heavier inert gas ions such as Kr. It has been observed that, while Kr ions have shallow penetration depths than Ar ions and therefore cause less surface damage, Ar ions remove C atoms from the surface more efficiently than Kr ions.

References

[1] A. Hirata, M. Fukasawa, K. Kugimiya, K. Nagaoka, K. Karahashi, S. Hamaguchi, and H. Iwamoto, *JVST A*, **38**, 062601 (2020).

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

3:20pm **AP+PS-MoA-6 Orientation Dependent Etching of Silicon: A Computational Chemistry Study**, ***Yuri Barsukov**, O. Dwivedi, S. Jubin, J. Vella, I. Kaganovich,* Princeton University Plasma Physics Lab

Orientation dependent etching of silicon is a phenomenon, when etch rate of silicon surface depends on the surface orientation. It was experimentally established that Si(111) surface is slower etched than Si(100) and Si(110). In this case the etch profile becomes anisotropic (without plasma and ions) and the surface is textured with micro- and nano-scale pits. In other words, anisotropy of the etching determines surface roughness. Plasma-less atmospheric dry etching is one of the applications of this processing in technology of black silicon production for photovoltaic solar cell manufacturing, where F_2 gas makes silicon surface rougher. On the other hand, rough surface is unwanted during manufacturing of integrated circuits, because it leads to degradation of device characteristics. Thus, basic understanding of this phenomenon is needed to better control surface structure during the etching.

We performed modeling of Si(100), Si(110) and Si(111) etching by F_2 molecule combined with DFT (density functional theory), TST (transition state theory) and MD (molecular dynamics) approaches like it was done in [1,2]. The combination of DFT and TST enables us to calculate probabilities of gas-surface reactions and perform kinetic modeling of the etching, while under MD approach evolution of the surface at different temperatures at ns time-scale is considered.

We assumed that F_2 dissociative chemisorption leading to Si-Si bond breaking is rate-determining step of whole etching process and reproduce the experimental measurements that the barrier of F_2 dissociation on Si(111) is significantly higher than on Si(100) and Si(110). We established that the value of the barrier is determined by the charge distribution on the surface, and the charge distribution in turn is determined by the number of F atoms incorporated into the surfaces.

Our modeling was validated and well reproduced experimental data such as values of activation barrier and etch rate as a function of temperature.

Based on our mechanism of the etching we will perform similar modeling aimed to design new etchants for Si etching to better control roughness and surface texturing.

References:

1. S Jubin et al, *Frontiers in Physics* 10, (2022) DOI: 10.3389/fphy.2022.908694.
2. Y Barsukov et al, *Nanotechnology* 32, 475604 (2021) DOI: 10.1088/1361-6528/ac1c20.

4:20pm **AP+PS-MoA-9 Process Drift of SiO_2 Atomic Layer Etching in HFC and FC/Ar Chemistries by Optical Spectroscopy and Surface Chemistry Analysis**, ***Antoine Ronco**[1], F. Boulard, N. Posseme,* Univ. Grenoble Alpes, CEA, Leti, France

Manufacturing new semiconductor devices requires atomic scale control of etching processes in order to decrease their dimensions. Atomic Layer Etching (ALE) allows such thin control of the processes [1][2]. One of the challenges is tuning the durations of the deposition and activation steps to obtain a process with a stable amount of material etched per cycle. If not tuned correctly the fluorocarbon (FC) film can accumulate on the sample's surface causing a drift in the amount of material etched per cycle (EPC)[3]. In this paper, we investigate the use of Optical Emission Spectroscopy (OES) to monitor the drift of a quasi-ALE process. Then, we study the impact of the gas chemistry on the appearance of the drift. Finally, we optimize contact hole etching and especially the landing on the etch stop layer.

The samples studied consist of 100 nm SiO_2 on Si blanket wafers. The experiments are carried out in a 300 mm capacitively coupled plasma reactor. The wafers are etched using C_4F_8, C_4F_6, or CH_3F/Ar based chemistry in a two steps approach, namely deposition and activation. The reactor is cleaned using an O_2 plasma before and after etching each wafer.

We observe a decrease in EPC of a quasi-ALE process when increasing the number of cycles. The examination of the evolution of the intensities of OES spectra through deposition and activation steps reveals that the line at 251 nm, which could correspond to CF/CF_2 radicals, is an indicator of the drift of the process [4]. The decreasing intensity observed during the activation step suggests the accumulation of a carbon film on the sample's surface. This is confirmed through XPS analysis showing an increase in carbon content on the sample's surface when increasing the number of cycles. The correlation between XPS analysis, OES observation, and EPC evolution with the number of cycle shows that the EPC drift can be monitored in real time using OES.

We use this method to study the impact of gas chemistry on the drift of our etching process for SiO_2 and SiN etching. The effect of the FC gas used on the selectivity and uniformity of our process is also reported.

Finally, the impact of gas chemistry and number of cycles on pattern etching is characterized using a Scanning Electron Microscope (SEM). Particular interest is paid to the conformality of the FC film deposited on patterns and etching at the bottom of the contact.

[1] K. J. Kanarik et al., JVSTA **33**, no 2, 020802, 2015

[2] G. S. Oehrlein, et al., ECS J. Solid State Sci. Technol. **4**, no 6, N5041–N5053, 2015

[3] C. M. Huard, et al., JVSTA **36**, no 6, 06B101, 2018

[4] R. W. B. Pearse, et al., The identification of molecular spectra, 4th ed. London: Chapman & Hall, 1976.

4:40pm **AP+PS-MoA-10 Atomic Layer Etching of Superconducting Titanium Nitride Thin Films Using Molecular Oxygen and H_2/SF_6 Plasma**, ***Azmain Hossain**, A. Minnich,* California Institute of Technology

Microwave loss in superconducting titanium nitride (TiN) films is attributed to two-level systems in various interfaces arising in part from oxidation and microfabrication-induced damage. Atomic layer etching (ALE) is an emerging subtractive fabrication method which is capable of etching with Angstrom-scale etch depth control and potentially less damage. However, while ALE processes for TiN have been reported, they either employ HF vapor, incurring practical complications; or the etch rate lacks the desired control. Further, the superconducting characteristics of the etched films have not been characterized. Here, we report an isotropic plasma-thermal TiN ALE process consisting of sequential exposures to molecular oxygen and an SF_6/H_2 plasma. For certain ratios of SF_6:H_2 flow rates, we observe selective etching of TiO_2 over TiN, enabling self-limiting etching within a cycle. Etch rates were measured to vary from 1.1 Å/cycle at 150 °C to 3.2 Å/cycle at 350 °C using ex-situ ellipsometry. We demonstrate that the superconducting critical temperature of the etched film does not decrease beyond that expected from the decrease in film thickness, highlighting the low-damage nature of the process. The ALE-treated films were also studied using XPS and AFM. These findings have relevance for applications of TiN in microwave kinetic inductance detectors and superconducting qubits. (arXiv:2307.02821)

5:00pm **AP+PS-MoA-11 Quasi-Atomic Layer Etching of X-Cut MgO-Doped Lithium Niobate Using Sequential Exposures of H_2 and SF_6 Plasma**, ***Ivy Chen**, J. Solgaard, R. Sekine, A. Hossain, A. Ardizzi, D. Catherall, A. Marandi,* California Institute of Technology*; F. Greer,* Jet Propulsion Laboratory (NASA/JPL), California Institute of Technology*; A. Minnich,* California Institute of Technology

Lithium niobate ($LiNbO_3$, LN) is an emerging platform for integrated photonics. Recent demonstrations of record on-chip quantum states, >100 GHz electro-optic modulators with CMOS compatible voltages, and multi-octave frequency combs with ~100 fJ pump pulse energies highlight the potential of this platform to enable novel on-chip photonic functionalities. However, thin-film lithium niobate (TFLN) devices suffer from large scattering losses resulting from the surface roughness left by Ar^+ milling, the standard technique used for nanophotonic LN waveguide fabrication, negatively impacting device performance. Atomic layer etching (ALE) can potentially mitigate scattering losses due to its ability to smooth surfaces to sub-nanometer length scales, but no ALE process has been reported for TFLN. Here, we report an anisotropic quasi-ALE process for X-cut MgO-doped LN using sequential exposures of H_2 and SF_6 plasma. We observe etch rates up to 2.1 nm/cycle with a synergy of ~97% and characterize the

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

etched surfaces using X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and atomic force microscopy. This process has the potential to serve as a post-processing step to smooth patterned TFLN surfaces which may both increase the performance of existing TFLN devices and enable novel devices not attainable in other integrated photonic platforms.

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+EM+PS+TF-TuM

Area Selective Processing and Patterning

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

8:00am **AP+EM+PS+TF-TuM-1 Area-Selective Deposition in Nanoscale Patterns*, Annelies Delabie,*** Imec Belgium, and KU Leuven Belgium*; J. Clerix,* IMEC Belgium*; K. Van Dongen,* IMEC, Belgium*; J. Sinha,* IMEC Belgium*; L. Nyns,* IMEC, Belgium*; R. Nye,* LAM Research*; G. Parsons,* North Carolina State University*; J. Swerts,* IMEC Belgium **INVITED**

Manufacturing nano-electronic devices becomes more and more complex as the device dimensions reach the nanoscale and a wide range of new materials is being implemented to achieve high device performance. Additional complexity comes from the use of three dimensional (3D) structures to reduce the active footprint. Area-Selective Deposition (ASD) provides a promising avenue to assist and/or even simplify device manufacturing processes. ASD is a technique to deposit material only on a pre-defined area of a patterned surface (the growth area), while no deposition is intended on other areas of the same surface (the non-growth area). As such, ASD can be used to replicate patterns on 3D substrates and to (partly) fill narrow trenches or holes from the bottom up. ASD can be achieved by tuning the adsorption and diffusion kinetics in atomic layer deposition (ALD) and chemical vapor deposition (CVD) processes. Insight in the chemical and physical processes is essential to enable rational design of new ASD processes for nano-electronic device manufacturing for advanced technology nodes.

This presentation will discuss the growth mechanisms during ASD on substrates that contain nanoscale patterns, where the geometry of the nanopatterns can affect the growth behavior, selectivity and uniformity. An aminosilane small molecule inhibitor can enable ASD on a wide range of materials with SiO_2 as the non-growth surface [1]. The selectivity of TiO_2 ALD relies mainly on adsorption. Selectivity loss during TiO_2ALD occurs via a nucleation site generation mechanism: small TiO_2 nanoparticles are continuously generated during ALD by slow, unintentional adsorption on the passivated non-growth surface area [2]. ASD super cycles consisting of inhibitor adsorption, TiO_2 ALD and etch effectively improve the selectivity, but may compromise the height uniformity in nanoscale patterns. The selectivity of Ru and $Ge_2Sb_2Te_5$ ALD relies on a complex interplay of adsorption, diffusion and aggregation. We reveal a pattern-dependent selectivity for Ru ALD, which is explained by aggregation of Ru adspecies at the pattern edges [3]. We conclude that the selectivity and uniformity of ALD processes can change when pattern dimensions reach the nanoscale.

[1] K. Van Dongen et al, *J. Vac. Sci. Technol. A* 2023, 41, 032404.

[2] R. A. Nye et al, *Appl. Phys. Lett.* 2022, 121, 082102.

[3] J.-W. J. Clerix et al, *Appl. Surf. Sci.* 2023,626, 157222.

8:40am **AP+EM+PS+TF-TuM-3 N-Heterocyclic Carbenes as Small Molecule Inhibitors in AS-ALD*, Cathleen Crudden,*** Queen's University, Canada **INVITED**

A unique carbon-based SMI, called an N-heterocyclic carbene (NHC), has been developed as a small molecule inhibitor using carbon as the heteroatom. NHCs have been used in organometallic and catalysis chemistry for decades, where they are renowned for their ability to form strong bonds to metal surfaces. We have developed a suite of organic SMIs with high volatility and thermal stability enabling deposition in an ALD tool. We demonstrated strong binding of the SMI to Ru, Co, Mo and Cu and selectivity for binding to metal surfaces in the presence of insulators. These results are informed by surface science studies including microscopy and spectroscopy.

9:20am **AP+EM+PS+TF-TuM-5 Unraveling Precursor Blocking Mechanisms in Area-Selective Atomic Layer Deposition Using Small Molecule Inhibitors*, Olaf Bolkenbaas,*** *M. Merkx,* Eindhoven University of Technology, Netherlands*; P. Yu,* eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Area-selective atomic layer deposition (ALD) has garnered significant attention as a potential technique for enabling the further miniaturization of semiconductor devices. One method for achieving area-selective ALD is through the use of small molecule inhibitors (SMIs) that selectively block deposition on certain materials. Previous research has indicated that precursor blocking by SMIs involves two components: the chemical removal of reactive surface sites and the physical blocking of the surface, also referred to as chemical passivation and steric shielding respectively [1]. However, it is difficult to differentiate between these two factors as they occur simultaneously. In this work we attempt to unravel the steric shielding and the chemical passivation contributions by the SMI acetylacetone (Hacac) with the use of reflection adsorption infra-red spectroscopy (RAIRS) on dehydroxylated Al_2O_3 surfaces obtained through annealing.

When comparing Hacac adsorption on an as-prepared and an annealed Al_2O_3 surface using RAIRS, a lower amount of Hacac adsorbates was observed on the annealed surface. Furthermore, a higher fraction of the Hacac adsorbates was present in the more strongly bonded chelate configuration. This difference in the distribution of the binding configurations demonstrates that the density of surface sites affects the SMI adsorption behavior. We expect that this different adsorption behavior is caused by a lower amount of steric hindrance between the SMIs on the annealed Al_2O_3 surface. Furthermore, the increase in the amount of adsorbates in the chelate configuration will result in a higher contribution of chemical passivation on the dehydroxylated surface, since only the adsorbates in the chelate configuration chemically passivate the surface [2]. From this we can conclude that the removal of surface sites can be used to obtain a better understanding of the two precursor blocking mechanisms. This better understanding will create opportunities for the development of new area-selective ALD strategies involving the removal of reactive surface sites before the functionalization with SMIs to improve selectivity.

[1] Merkx, et al., Chem. Mater. **32**, 3335–3345 (2020).

[2] Mameli et al., ACS Nano **11**, 9303–9311 (2017).

9:40am **AP+EM+PS+TF-TuM-6 Topographically-Selective Deposition Using Amorphous Carbon as Inhibition Layer*, Thijs Janssen,*** *M. Merkx, W. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

To accommodate the increasing complexity of device architectures in nanoelectronics, new nanoscale processing techniques are required. Selective deposition techniques have been developed in recent years to enable bottom-up and self-aligned processing[12]. While traditional area-selective deposition distinguishes between areas depending on their chemical character, topographically-selective deposition (TSD) distinguishes between areas based on their orientation within a 3D structure[2,3]. Such TSD approaches offer new fabrication opportunities, for example when the growth and non-growth areas possess similar material properties, or when too many different materials are present within the device structure. Previously reported TSD methods have been demonstrated only for specific materials.

In our work, we develop a versatile TSD strategy that is potentially suitable for a broad range of materials. Our approach utilizes a pulsed Ar/CH_4 plasma to selectively apply an amorphous carbon (aC) inhibition layer on horizontally-oriented surfaces by relying on the directional ions from the plasma. The vapor-phase selective deposition of aC is integrated together with existing ALD processes and plasma treatments into a TSD supercycle recipe.

The highly inert surface of aC lacks suitable absorption sites for ALD precursors and co-reactants, making it an effective inhibition layer. It was found that only the horizontally-oriented surfaces are covered by the aC layer, thus subsequent ALD of target materials proceeds exclusively on vertically-oriented surfaces.

Successful ALD inhibition on the aC surface is established for several different target materials such as TiO_2 using TDMAT and H_2O, Nb_2O_5 using TBTDEN and H_2O, and NiO_x using $Ni(BuAMD)_2$ and H_2O. In particular 90% selectivity was maintained for 35 cycles TiO_2 deposition (1.09 ± 0.01 nm selective growth), 70 cycles Nb_2O_5 deposition (4.38 ± 0.02 nm) and 40 cycles of NiO_x deposition (1.28 ± 0.01 nm). It is demonstrated for NiO_x that the supercycle can be repeated, which effectively resets the nucleation delay, such that a thicker film (nominally ~5 nm after 4 supercycles) can be deposited selectively.

1. Mackus, A. J. M., Merkx, M. J. M. & Kessels, W. M. M. From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity. *Chem. Mater.***31**, 2–12 (2019).
2. Parsons, G. N. & Clark, R. D. Area-Selective Deposition: Fundamentals, Applications, and Future Outlook. *Chem. Mater.***32**, 4920–4953 (2020).

3. Chaker, A. *et al.* Topographically selective deposition. *Appl. Phys. Lett.***114**, (2019).

11:00am **AP+EM+PS+TF-TuM-10 A ReaxFF Study for Hacac Interaction on Al_2O_3 Surface in Area-Selective ALD***, **Naoya Uene,*** Tohoku University, Japan*; I. Tezsevin, W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands*; A. van Duin,* Pennsylvania State University*; T. Tokumasu,* Tohoku University, Japan

An area-selective ALD process of SiO_2 was developed comprising acetylacetone inhibitor (Hacac), bis(diethylamino)silane precursor (BDEAS), and O_2 plasma reactant pulses. Hacac inhibitors lead to delayed SiO_2 growth on the Al_2O_3 surface for about 15 ALD cycles, after which the selectivity is lost. Two chemisorption configurations of Hacac inhibitors on Al_2O_3 surfaces have been reported: monodentate and chelate configurations. (Merkx et al. 2020) Density functional theory (DFT) calculations have shown that the monodentate configuration is relatively reactive with incoming BDEAS, causing the loss of selectivity due to precursor-inhibitor reactions. Therefore, exploration of the relative densities of the chelate/monodentate configurations on the surface is crucial for the understanding of the selectivity loss mechanism. We aim to understand the reaction mechanisms of Hacac inhibitor adsorption on Al_2O_3 surfaces at the atomic scale.

Up to now, the investigation of the adsorption of inhibitor molecules has been studied via DFT calculations. Thereactive force-field molecular dynamics (ReaxFF MD), which can simulate chemical reactions and physical dynamics at the atomic scale, has been used for gas-surface systems. (van Duin et al. 2001) We performed ReaxFF MD simulations to consider the chemical reactions of Hacac inhibitor molecules with dislocation effects on the surface. An initial force field has been developed for the Hacac interaction on Al_2O_3 surface based on the two existing force fields: Li/Si/Al/O force field for Al_2O_3 structure and protein force field for carbohydrate interactions. (Kim et al. 2016; Monti et al. 2013) The initial force field is trained for Hacac geometry, and their reaction on an OH-terminated Al_2O_3 surface is also modeled.

We performed ReaxFF MD simulations using the developed force field. The simulation consists of three steps. First, the Al_2O_3 surface is pre-thermally relaxed. Then, the Hacac inhibitor is supplied on the relaxed surface, followed by post-thermal relaxation of the Hacac-adsorbed surface. We first confirmed the temperature stability of the Al_2O_3 surface with different temperatures. Our force field can control the temperature of the Al_2O_3 surface ranging from 300 K to 1500 K. Next, sequential adsorption of 20 Hacac inhibitor molecules was simulated on the temperature-controlled Al_2O_3 surface, as shown in the supplemental document. The findings from our ReaxFF simulations provide in-depth insights into the mechanisms of Hacac adsorption and saturation on the surface. These insights will be used for the investigation of precursor blocking and blocking selectivity loss in our future work.

11:20am **AP+EM+PS+TF-TuM-11 Enhancement of TMSDMA Passivation on SiO2 by Surface Fluorination***, **Anthony Valenti,*** SUNY College of Nanoscale Science and Engineering*; C. Vallée,* SUNY College of Nanoscale Science and Engineering, France*; C. Ventrice,* SUNY College of Nanoscale Science and Engineering*; K. Tapily, K. Yu, S. Consiglio, C. Wajda, R. Clark, G. Leusink,* TEL Technology Center, America, LLC, USA

With the ever-shrinking scale of semiconductor devices, area-selective atomic layer deposition (AS-ALD), a bottom-up and self-aligned patterning process with atomic-scale control has been in development in order to meet the demands of industry. This technique is typically conducted by promoting growth on specific surface termination types, while inhibiting growth on the other surface types of the substrate via selective chemisorption of molecules that are inert to the deposition process. With its affinity for chemisorbing to hydroxylated oxide surfaces, specifically SiO2, but not on Si or non-oxidized metal surfaces, N-(trimethylsilyl)dimethylamine (TMSDMA) has been of recent interest for its use as a small molecule inhibitor (SMI) for area selective deposition (ASD). Upon interaction with a surface hydroxyl group, the TMSDMA molecule dissociates, resulting in a trimethylsilyl group bonded to the chemisorbed oxygen atom of the hydroxyl group. Although TMSDMA-passivated SiO2 typically remains inert over several ALD cycles, nucleation of the growth precursor can eventually occur. This may be due to hydroxyl groups on the surface that did not interact with TMSDMA molecules and/or non-hydroxylated sites that were not passivated by trimethylsilyl groups. For instance, surface siloxane bridges do not dissociate TMSDMA and can act as nucleation sites for the ALD growth precursor. In order to enhance the passivation of SiO2 surfaces, the use of co-passivants has been explored. In particular, a remote NF3 plasma has been studied as a means for forming a co-inhibitor. Dosing before or after TMSDMA treatment has been investigated. The deposition of the small molecules were carried out on 10 Å SiO2/Si(100) substrates. Water contact angle measurements were taken to determine relative surface passivation of each sample. Angle-resolved X-ray photoelectron spectroscopy and attenuated total reflection/Fourier transform infrared spectroscopy were performed in order to characterize the chemical state of each surface. Our results indicate that exposure of the substrate to the NF3 plasma after passivation with TMSDMA, results in damage to the passivating layer. However, exposure of the surface to the NF3 plasma before TMSDMA exposure maintains the passivation of the SiO2 surface. In addition, temperature programmed desorption (TPD) measurements are being conducted to assess the relative coverage of the inhibiting film on each sample and its thermal stability.

11:40am **AP+EM+PS+TF-TuM-12 A Study of Elucidation and Improvement of TiO_2 Selectivity by First-Principles Based Thermodynamic Simulation***, **Yukio Kaneda,*** Sony Semiconductor Solutions Corporation, Japan*; E. Marques, S. Armini, A. Delabie, M. van Setten, G. Pourtois,* IMEC, Belgium **INVITED**

Area-selective deposition (ASD) enables the deposition of materials in a targeted area, typically a pre-patterned surface, while preventing the growth on adjacent surfaces.[1] The technique is appealing for both academia and industry as it offers a vehicle to simplify material developments in nanoelectronics. Consequently, numerous efforts have been dedicated to investigate the factors driving the selectivity mechanisms and to identify optimal process deposition conditions, including surface treatments, that enable highly selective processes.

The "selectivity" dimension results from the identification of the right combination of precursors (including co-agents), surface treatments, and reactor operating conditions. This is typically a complex and laborious process that requires many systematic and tightly controlled experiments. As a result, the development of highly selective ASD processes is often a slow and challenging task where any form of guidance provided by modeling insights can be precious.

In this context, we studied, by combining thermodynamic considerations and first principle simulations, the reactivities of complex surface chemical reaction networks and the factors impacting on selectivity. In this talk, we will discuss the case of the ASD of TiO_2 on SiO_2 substrates terminated with either "reactive" (-OH) or "passivated" alkyl-silyl groups. First, we will first briefly discuss the validation of our approach by comparing our model prediction with experimental measurements for the case of the ALD of TiO_2 using the precursors $TiCl_4$ and $Ti(OMe)_4$ and then report the insights gained for the identification of optimum Ti precursor and inhibitor for the ASD of TiO_2. We will then extend the discussion to the case of the ASD supercycles of TiO_2, where the interaction of some Ti precursors (or of their ligands) leads to the degradation of the surface "passivation" and then requires restoring the surface by injecting of alkyl-silyl functional groups. We will review the strategies that worked with their drawbacks.

[1] Gregory N. Parsons and Robert D. Clark, Chem. Mater. **2020**, 32, 12, 4920–4953

[2] Job Soethoudt, *et al.,The Journal of Physical Chemistry C***2020***124* (13), 7163-7173

[3] Janne-Petteri Niemelä *et al.,Semicond. Sci. Technol.***2017** 9 (32), 093005

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP1+2D+EM+PS+TF-TuA

Atomic Layer Processing: Integration of Deposition and Etching

Moderator: John F. Conley, Jr., Oregon State University

2:20pm **AP1+2D+EM+PS+TF-TuA-1 Combination of Plasma-Based Atomic-Scale Deposition and Etching Processes for Advanced Patterning*, Marceline Bonvalot,*** LTM - MINATEC - CEA/LETI, France*; C. Vallée,* SUNY College of Nanoscale Science and Engineering*; r. gassilloud, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France*; N. Posséme,* STmicroelectronics, France **INVITED**

Selective Deposition processes have gained increased research interest in recent years, because they enable the accurate placement of a thin film on a specific substrate surface (in the case of area selective deposition ASD) or on specifically oriented surfaces (in the case of topographical selective deposition TSD). Such processes require atomic-scale precision, and usually involve Atomic Layer Deposition techniques, with possibly plasma assistance. Several pathways have been proposed in the literature for ASD, most commonly implying surface inhibition treatments with dedicated chemical treatments (self-assembled molecules or small molecule inhibitors for instance) to increase the nucleation delay during the subsequent ALD growth. However, the dedicated inhibition behavior eventually deteriorates when exposed to a few ALD cycles, which requires that on the one hand, nuclei formed on non-growth surfaces be removed and on the other hand, the inhibitor be systematically regenerated.

In this presentation, we will show how the insertion of an *in situ* etching step in the overall ALD process can serve as an effective corrective treatment for this purpose. The etching periodicity in conventional deposition/etching duty cycles will be investigated in details. We will show that the etching step should preferentially be carried out before the transition from the Volmer-Weber 1D island growth mode to the 2D layer by layer growth mode on non-growth surfaces, to limit plasma-induced surface defects. Moreover, the 1D island growth mode seems to coincide with the onset of degradation for the surface inhibition treatment. In this context, it will be shown that the etching periodicity is a determining parameter for the successful development of a selective bottom-up growth strategy.

3:00pm **AP1+2D+EM+PS+TF-TuA-3 Application of Etching Reaction Models to Deposition Processes*, Nobuyuki Kuboi,*** Sony Semiconductor Solutions Corporation, Japan **INVITED**

Advanced CMOS devices require highly intricate 3D stacked structures with varying aspect ratios such as FinFETs and GAAs [1]. Understanding the process properties of plasma etching [2] and deposition [3] processes based on their mechanism and combinations has become increasingly important in addressing this challenge. Additionally, microfabrication properties should be stably suppressed within a specific range during mass production. However, the monitoring system equipped in the process chamber is limited for mass production. Therefore, we propose predictive models for plasma etching and deposition that consider the physical and chemical aspects of the plasma and surface.

First, we briefly introduce simulations for fluctuations in the SiN etching rate influenced by the chamber wall condition, critical dimensions during Si gate etching caused by $SiBr_x$ by-products dependent on open area ratios on wafer/chip/local-pattern levels, damage distribution affected by local-pattern structure, ion energy, and hydrogen concentration in the SiO_2 and SiN films, and selectivity during SiO_2-ALE [4][5][6].

We then present a modeling and simulation of the deposition process as a motif of the SiN-PECVD process using a 3D voxel method that can be associated with the previous process, such as plasma etching [7]. The model can predict film properties as well as the coverage on a large-scale pattern. Reactions among voxels are considered pseudo treatments for atomistic interactions on the surface. A statistical ensemble method involving probabilities is used to express physical and chemical phenomena such as sticking, migration, and bond formation on the deposited surface. The sticking and bond probabilities are affected by surface damage and IEADFs, respectively. Our model can successfully reproduce the experimental characteristic relationship between the morphology and film density dependent on the SiH_4 flow rate during the low temperature (120 ºC) SiN-PECVD process considering different gas residence times that affect surface reactions. Furthermore, we discuss the issue of modeling the ALD process.

These simulation technologies can aid in optimizing the chamber wall condition, pattern design, and etching/deposition combination process.

[1] N. Singh *et al*., IEEE Electron Device Lett. **27**, 383 (2006).

[2] T. Tatsumi *et al*., Jpn. J. Appl. Phys. 61, SA0804 (2022).

[3] H. C. M. Knoops *et al*., J. Vac. Sci. Technol. A **37**, (2019) 030902.

[4] N. Kuboi *et al*., Appl. Phys. Express **5**, (2012) 126201.

[5] N. Kuboi *et al*., J. Vac. Sci. Technol. A **35**, (2015) 061306.

[6] N. Kuboi *et al*., J. Vac. Sci. Technol. A **37**, (2019) 051004.

[7] N. Kuboi *et al*., Jpn. J. Appl. Phys. **62**, (2023) SI1006.

4:20pm **AP1+2D+EM+PS+TF-TuA-7 Recent Advancements for Atomic Layer Advanced Manufacturing Processes: Microreactor Direct Atomic Layer Processing (µDALP™)*, Maksym Plakhotnyuk,*** *A. Varga, I. Kundrata,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann,* ATLANT 3D Nanosystems; Friedrich-Alexander Universität Erlangen-Nürnberg, Denmark **INVITED**

As the demand for miniaturized and complex devices continues to grow across various industries, the need for innovative and precise atomic layer advanced manufacturing (ALAM) technologies becomes increasingly apparent[1]. Our company, utilizing proprietary Microreactor Direct Atomic Layer Processing (µDALP™), is at the forefront of pushing sALD's capabilities and broadening its application horizons. The µDALP^{TM} process undergoes the same cyclic ALD process but only in a spatially localized area.[2] The microreactor or micronozzle confines the flows of gases used for ALD within a defined µm-scale centric area on the substrate to deposit the desired material.[3]

ATLANT 3D's recent advancements in our novel µDALP™ technology have enabled innovation within the thin film deposition field ranging from ALD material development to rapid prototyping and manufacturing. The µDALP™ process enables multiple depositions e.g., depositions with varying film thicknesses, to be deposited onto a single wafer used to calculate a given processes growth rate within only a few hours, compared to days for a traditional ALD process. In Addition, innovation of applications including optics and photonics, quantum devices, MEMS, RF electronics, emerging memory technologies, advanced packaging, and energy storage are possible and have been demonstrated using µDALP™ technology.

Discussing the improvements to the µDALP™ process, we have decreased the process resolution, increased material compatibility, and accessible morphologies. Giving one example of the recent development in morphologies, films deposited with µDALP™ have conformal coverage of gratings, microchannels, and trenches up to a depth of 25 µm using a Platinum deposition process. **Fig. 1** demonstrates how a given ALD material process (in this case, Pt) can be used with ATLANT 3D technology to deposit localized area conformal coatings of complex surfaces with an aspect ratio of 1:25. Hence demonstrating the versatility and potential of our technology for achieving inherently selective ALD for processing on complex surface morphologies.

This talk aims to shed light on how our breakthroughs in spatial ALD and µDALP™ technology contribute to the advancement of ALAM and scale-up. Fostering a deeper understanding of our technology's capabilities and exploring the possibilities it opens up for various industries.

[1] Poodt P., *JVSTA.*, **2012**, *30*, 010802

[2] Kundrata I., et al., *Small Methods.*, **2022**, *6 (**5**)*, 2101546

[3] Plakhotnyuk M, et al., *ALD/ALE 2022 [Int. Conf.]*,**2022**

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP2+PS+TF-TuA

Energy Enhanced ALD

Moderator: John F. Conley, Jr., Oregon State University

5:00pm **AP2+PS+TF-TuA-9 Atomic Layer Annealing with Radio Frequency Substrate Bias for Control of Grain Morphology in Gallium Nitride Thin Films***, A. Mcleod, P. Lee,* University of California, San Diego*; S. Yun, S. Ueda,* University of California, San Diego, USA*; Z. Devereaux, C. Winter,* Wayne State University*; J. Spiegelman,* RASIRC*; R. Kanjolia, M. Moinpour,* EMD Electronics, USA*;* ***Andrew Kummel,*** University of California, San Diego **INVITED**

Low temperature GaN deposition is critical for passivation layers on nitride power FET as low as templating and capping layers on sputtered AlN films for heat spreader. A method of performing atomic layer annealing with RF substrate bias on insulating and amorphous substrates is demonstrated for GaN deposition at 275 ℃. GaN is typically deposited by MOCVD or MBE at >600 ℃, resulting in strain upon cooling; this makes low temperature process alternatives desirable. Tris(dimethylamido) gallium (III) and hydrazine served as precursors while Ar and Kr were used for ion bombardment. Optimization of substrate bias potential is demonstrated by GI-XRD and XRR. Reference films were deposited by thermal ALD and non-substrate biased ALA processes. XPS surface and depth-profiling studies show that applied RF bias decreases film oxygen and carbon content relative to the reference films; these films also show crystallites broadening with increasing film thickness by TEM in contrast to the reference films. In summary, ALA with RF substrate bias is demonstrated as an effective method to deposit GaN thin films at a low deposition temperature on insulators.This technique has recently been expended to growth of InGaN films which applications in microLEDs.

5:40pm **AP2+PS+TF-TuA-11 Atomic Layer Annealing for sub-10 nm, Wake-up Free Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films***,* ***Yu-Sen Jiang,*** National Taiwan University, Taiwan*; T. Chang, S. Yi,* Taiwan Semiconductor Manufacturing Company, Taiwan*; M. Chen,* National Taiwan University, Taiwan

Conventional annealing techniques pose significant challenges in nanoscale fabrication. One prominent issue involves the heating depth, which typically exceeds the critical dimension of nanoscale devices. Consequently, conventional annealing methods introduce excessive thermal budget, resulting in performance degradation of the devices. Atomic layer annealing (ALA) is capable of adjusting the film quality at the atomic level during low-temperature (300℃) deposition without the need for any post-annealing process, which tremendously lowers the thermal budget and can tailor the film properties as required. In this report, the ALA technique was used to realize sub-10 nm wake-up free ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films with high remnant polarization and low thermal budget. The HZO thin films have also been used as gate dielectrics in junctionless transistors, demonstrating steep subthreshold swing (< 60 mV/decade) in nanoscale devices. The outcome manifests the remarkable capabilities of ALA in enabling precise engineering and fabrication of nanoscale materials and devices.

6:00pm **AP2+PS+TF-TuA-12 A System for Predicting the Area Selective Deposition of Titanium: Plasma State Diagnostics Using Electrical Simulation***,* ***Kyoungmi Choi****, T. Hong, H. Kim, Y. Oh,* Samsung Electronics Co., Inc., Republic of Korea

The selective deposition of thin films in specific areas is crucial for achieving the desired size and lowresistance of semiconductors. Due to differences in chemistry between molecule/surface and molecule/vapor interactions, thin films are selectively deposited on pre-patterned substrates. Although simulations have been used to predict Ti film thickness using plasma simulation and surface reaction models, the effect of selective deposition on the pattern was not studied. In this study, an electrical simulation was used to predict the selectivity of the area selective deposition process on the patterned wafer.

To identify the main factors affecting selectivity, we reviewed the plasma temperature and density. Plasma density can be indirectly inferred from the output current of the matcher. Another factor that influences selectivity is plasma temperature, specifically the electron temperature [eV]. The sheath voltage is proportional to the electron temperature. Therefore, we established an electric simulation system (Fig. 1) to estimate the sheath voltage. The CCP consists of an RF generator, a matcher, and a chamber. We identified the matcher parameters (C_{tune}/C_{load}/L) using the maximum power transmission theory, assuming that the chamber was $Z_{chamber}$(Fig 2). The model was verified using MATLAB and the sheath voltage was derived using the matcher and bottom currents. The simulations and evaluations of pressure/RF power/impedance were performed. The validity of the electrical model was confirmed by comparing the simulation and the experimental current.

To verify the simulation, Ti deposition experiments were conducted on Si/SiO wafers under 7 conditions (Table1). The simulation results for sheath voltage and the experimental results for deposition rate showed a correlation of 0.77, and the Si/SiO selectivity showed a correlation of 0.92(Fig 3).

Through the correlation result,itwasderivedasthefollowingconclusion.The correlation results between sheath voltage and the area selective deposition explains the difference in the activation energy of the Si/SiO surfaces: The Si-Si bonding energy is 3.39 eV and the Si-O bonding energy is 8.29eV (Fig 4). Since there are regions where the plasma temperature is active on Si and inert on SiO, they are selectively deposited. Therefore, a sheath voltage simulation can be used to predict the selectivity. With further development, this simulation can be applied to other deposition equipment that uses plasma, and trends in process results for other process parameters that are sensitive to plasma temperature can be inferred.

Atomic Scale Processing Mini-Symposium
Room Oregon Ballroom 203-204 - Session AP-TuP
Atomic Scale Processing Poster Session

AP-TuP-2 in-Situ Laser Diagnostics of Plasma Surface Interactions by fs-TALIF*, **Mruthunjaya Uddi,*** Advanced Cooling Technologies*; A. Dogariu,* Texas A&M University*; E. Kudlanov,* Advanced Cooling Technologies*; G. Urdaneta,* Texas A&M University*; Y. Xiao, D. Jensen, C. Chen,* Advanced Cooling Technologies

Plasma surface interaction has been a critical area of research for many applications such as Plasma-Enhanced Atomic Layer Deposition (PEALD). To meet the demanding needs of more advanced atomically controlled microfabrication methods, the physics of PEALD needs to be better understood to enable high quality, repeatable and controllable deposition process. Several challenges that need to be addressed regarding PEALD include damage to the substrate from highly energetic species and UV radiation, need for precise amorphous/crystalline modulated selective layer deposition, conformality in coating non-uniform substrates, achieving an aspect ratio of >100, repeatability and controllability of the finish. To address these challenges, we are developing laser diagnostics methods to measure species over substrates by advanced laser diagnostics such as femtosecond- Two-Photon Absorption Laser Induced Fluorescence (fs-TALIF) to image atomic species over substrates. Here we present measurements of N atom densities over a substrate with high spatial (< 10 microns) and temporal resolution (<1 ns) using fs-TALIF at pressures of 5-150 mTorr.

AP-TuP-3 Characteristics of Hydrogenated Amorphous Carbon Thin Films Fabricated by Plasma-Enhanced Chemical Vapor Deposition of Cyclohexane Precursor*, T. Poche, R. Chowdhury, **Seonhee Jang,*** University of Louisiana at Lafayette

The characteristics of the hydrogenated amorphous carbon (a-C) films can be determined by the composition of sp^3, sp^2, and *sp*hybridized structures depending on the bond type of four valence electrons. The C-C bonds with sp^3, sp^2, and *sp* correspond to diamond, graphite/graphene, and carbyne, respectively. Mixed hybridization determines different carbon allotropes such as graphyne (*sp* and sp^2), nanotube and graphene quantum dots (sp^2 with sp^3), fullerene (sp^2 and sp^3), carbon dots (sp^3 with sp^2), and yne-diamond (*sp* and sp^3). Different mechanical, electrical, chemical, and optical properties are obtained depending on the mixture of sp^3, sp^2, and *sp*. For example, the sp^3 bond shows some advantages including mechanical strength, wide band gap, and chemical and electrochemical inertness, however it is unfavorable for a strip process after etching. The a-C films are characterized according to the composition ratios among a sp^3, sp^2, and hydrogen. When the hydrogen content is large, polymer-like a-C films can be formed with low film density due to high content of sp^3. When the hydrogen content is small, the content of sp^3 becomes low, resulting in a diamond-like a-C with high film density and hardness. When the hydrogen content becomes smaller, the content of sp^2 is high and a graphite-like a-C can be obtained. Depending on the deposition conditions, the sp^2/sp^3 hybridization ratio can vary over a wide range of values. The a-C thin films were fabricated by plasma-enhanced chemical vapor deposition (PECVD) of cyclohexane (CHex, C_6H_{12}) precursor. The a-C films were deposited at room temperature of 25 °C with a pressure of 26.7 Pa. The RF plasma power with 13.56 MHz was chosen from 20 to 80 W. The thickness, refractive index, and extinction coefficient of the a-C films were measured by ellipsometer. Surface morphology and roughness of the films were observed by atomic force microscopy (AFM). The functional groups of the films were identified using Fourier transform infrared (FTIR) spectroscopy. The FTIR spectrum consisted of C-H stretching, C-C stretching, and C-H bending modes. The $C-H_x$ stretching peak at 3100-2800 cm^{-1} was deconvoluted to determine the bonding structure of hydrogen in the a-C films and the fractions of sp^3 CH_2 stretching and sp^3 CH_3 stretching modes was investigated depending on deposition parameters. The structural arrangement of the carbon bonds was analyzed by Raman spectroscopy and showed E_{2g} G and A_{1g} D breathing modes. The chemical composition of the films was determined by X-ray photoelectron spectroscopy (XPS). The deconvoluted C1s revealed sp^2 C=C and sp^3 C-C bonding peaks along with oxygen functional groups of C-O, C=O, and O-C=O.

AP-TuP-4 Fabrication Related Impurities Study of Aluminum Transition Edge Sensors*, **Ghadendra Bhandari,*** West Virginia University*; T. Stevenson, E. Barrentine,* NASA*; M. Holcomb,* West Virginia University

Superconducting aluminum-based microwave kinetic inductance detectors (MKID) are being developed to be used in space technology. These detectors operate at extremely low temperature regime which improves signal to noise ratio.We have studied the residues and adsorbates during different stages of the device preparation processes using x-ray absorption spectroscopy (XAS). We have observed oxidation and fluorination of aluminum during the fabrication process. We have observed aluminum oxidize as a-Al_2O_3 phase and fluorination at AlF_3. Additionally, we studied the effectiveness of residue removal processes with the help of reference samples.

AP-TuP-5 Plasma-Induced Surface Defects and Their Impact on the Surface Chemistry of Silicon Nitride and Silicon Carbonitride*, **Ting-Ya Wang**, G. Hwang,* University of Texas at Austin

As integrated circuits continue to shrink, the challenge of resistive-capacitive (RC) delay is becoming increasingly prevalent. Implementing low-κ dielectric materials using techniques such as atomic layer deposition (ALD) has become a popular approach to decreasing capacitance and improving film conformality. However, there are still many technical challenges that need to be addressed. Although plasma is widely used in semiconductor processing, it can negatively impact the achievement of high-quality low-κ materials.

A thorough understanding of surface structure and reactivity is essential. Currently available experimental methods are rather limited in their ability to study reaction mechanisms and non-invasively observe surfaces at the atomic level. Therefore, we have utilized computational methods, such as density functional theory (DFT) and Monte Carlo (MC), to investigate the underlying mechanisms of ALD, with a focus on silicon nitride (SiN) and silicon carbonitride (SiCN) thin films.

Based on DFT calculations, we have identified several active sites induced by plasma irradiation. For N_2 plasma treatment, previous studies are mainly focused on under-coordinated sites such as >Si=N- site, while other potential surface sites remain incompletely understood. Our work demonstrates that N_2 dimers can also act as reactive sites towards Si precursors. Moreover, we have found that under-coordinated Si and N defects can exhibit different electronic states and thus significantly different reactivity. In addition, plasma treatment can trigger bridging reactions that produce Si-N=C=N-Si bridges, which could also be active sites.

Different types of precursors, depending on the presence of carbon and chlorine, are commonly used to grow SiN or SiCN thin films. However, experimental studies have shown that precursors have different favorability over the reactive surfaces created by different plasmas. To better understand the phenomena, we have investigated the mechanisms underlying the reactions between various surface defects and these precursors. Moreover, we will also briefly touch our recent efforts of using DFT results as input data for MC simulations to investigate the coverage of these surface defects and how they affect the surface chemistry involved in plasma-enhanced ALD.

AP-TuP-6 Electron Heating Mode Changes in Plasma Sources Used for Atomic Precision Processing*, **David Boris,*** U.S. Naval Research Laboratory*; M. Johnson,* Huntington Ingalls Industries*; J. Woodward, V. Wheeler, S. Walton,* U.S. Naval Research Laboratory

The inclusion of plasma in plasma enhanced atomic layer deposition (PEALD) applications generally offers the benefit of substantially reduced process temperatures, greater flexibility in tailoring the gas-phase chemistry to produce desired film characteristics, and the ability to affect film crystallinity and phase.

Many PEALD systems use inductively coupled plasma (ICP) sources in materials synthesis.These sources can undergo changes in electron heating modes which can be induced by changes in applied power, pressure, or gas phase chemistry. Generally, these mode changes cause substantial variations in the electron energy distribution function and plasma density, which can impact the delivery of reactive and energetic species to substrates. This presentation explores the effects of heating mode changes on reactive species production and downstream plasma parameters (electron temperature, plasma potential, and plasma density).We discuss the use of probes and optical emission spectroscopy to characterize changes in the plasma parameters and how these changes affect the delivery of reactive and energetic species to the material surface. The discussion will include the results from select processing applications, where changes in plasma properties are linked to differences in material properties.This work supported by the Naval Research Laboratory Base program

AP-TuP-7 $NaHF_2$ as an Alternative Hydrogen Fluoride (HF) Source for Thermal Atomic Layer Etching and Deposition

Marcel Junige, *R. Hirsch, V. Ghodsi, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) and deposition (ALD) are defined by an alternating sequence of separate, self-limiting surface reactions. ALE modifies and volatilizes a thin film surface, thereby removing ultra-thin layers of material. ALD adsorbs a precursor and, depending on the co-reactant, adds ultra-thin layers of film material. ALE and ALD processes have been developed for a wide range of film materials, including metals and semiconductors, as well as their oxides, nitrides, and fluorides. ALE and ALD provide precise control of shrinking critical dimensions, conformality in complex 3D structures, and wafer-scale uniformity.

A vital step for ALE and ALD is the fluorination reaction using hydrogen fluoride (HF). For example, thermal ALE of alumina (Al_2O_3) cycles between HF to fluorinate and trimethylaluminum (TMA) to ligand exchange at elevated temperatures. Thermal ALD of aluminum fluoride (AlF_3) also cycles between TMA adsorption and HF to remove methyl groups and form AlF_3 below 250℃. One problem with HF is that its toxicity presents a challenge to health and safety. To address safety concerns, solvents may reduce the HF vapor pressure. For example, a 70% HF in 30% pyridine solution, commonly known as Olah's reagent, is used by organic chemists for fluorination reactions.

Other thermal ALE processes have also widely employed HF-pyridine. However, care is required during handling in a glovebox. Further difficulties are encountered in cleanup and waste management. To address these issues, this study tested sodium bifluoride ($NaHF_2$), a salt that was safer to handle because $NaHF_2$ exhibits negligible HF vapor pressure at room temperature. When heated to 150℃, $NaHF_2$ delivered HF vapor pressures up to 15 Torr. In addition, this solid salt was easier to clean up and reduced waste.

HF volatilization was observed by temperature-ramped quadrupole mass spectrometry. ALE experiments were conducted in a hot-wall, viscous-flow vacuum reactor equipped with an *in situ* spectroscopic ellipsometer. Thermal Al_2O_3 ALE using sequential HF/TMA exposures served as a standard reference to evaluate $NaHF_2$. HF from $NaHF_2$ exhibited diffusion-limited fluorination of Al_2O_3 and an etch per cycle consistent with previous results using HF-pyridine. X-ray photoelectron spectroscopy detected no sodium on the surface after ALE, indicating that sodium fluoride remained in the source cylinder. These studies indicated that $NaHF_2$ can be considered as an alternative HF source for fluorination reactions in thermal ALE or ALD on the laboratory scale.

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+PS+TF-WeM

Plasma Deposition and ALD Processes for Coatings and Thin Films

Moderators: Silvia Armini, IMEC, Belgium, **Jessica Kachian**, Intel Corporation

8:00am **AP+PS+TF-WeM-1 Recent Progress in Analysis of the Conformality of Films by Atomic Layer Deposition*, Riikka Puurunen,*** Aalto University, Finland **INVITED**

Conformality is a fundamental characteristic of atomic layer deposition (ALD) thin film growth technique. “Conformal” film refers to a film that covers all surfaces of a complex three-dimensional substrate with everywhere the same thickness and properties. ALD - invented independently by two groups in 1960s and 1970s - has since late 1990s been transformational in semiconductor technology. Apart from semiconductors, conformal ALD films find applications and interest in widely varied fields such as microelectromechanical systems, pharmaceutical powder processing, optical coatings, battery technologies and heterogeneous catalysts.

Conformality follows directly from the “ideal ALD” principles: growth of material through the use of repeated separate self-terminating (i.e., saturating and irreversible) gas-solid reactions of at least two compatible reactants on a solid surface. Obtaining conformality in practice is not self-evident, however. Reasons for deviation from conformality are multiple, ranging from mass transport limitations to slow reaction kinetics and various deviations from ideal ALD (e.g., by-product reactivity or a continuous chemical vapor deposition (CVD) component through reactant decomposition or insufficient purging). Incomplete conformality can also be intentional: a saturation profile inside a feature can be exposed, to enable an analysis of kinetic parameters of the reactions.

This invited talk will explore recent progress especially by the author and collaborators in understanding ALD conformality and kinetics, obtained via experiments and simulations. Experiments have been made with the recently commercialized (chipmetrics.com) silicon-based PillarHallTM lateral HAR test chips (channel height ~500 nm) and spherical mesoporous high-surface-area materials (average pore diameter ~10 nm, sphere diameter ~1 mm). Simulations are presented for 1d feature-scale models and optionally a recently developed 3d code for spheres. Two codes are available on GitHub: DReaM-ALD (diffusion-reaction model, DRM) and Machball (ballistic transport-reaction model, BTRM). Often it is assumed that diffusion during an ALD process in HAR features is by Knudsen diffusion and free molecular flow conditions prevail (Kn >>1). If so, a characteristic “fingerprint saturation profile” can be obtained, and the slope method (derived for DRM-ALD-Arts, GitHub) can be used to back-extract the lumped sticking coefficient. When diffusion is in the transition flow (Kn ~1) or continuum flow (Kn<<1), the shape of the saturation profile depends on process conditions and the slope method is not applicable.

8:40am **AP+PS+TF-WeM-3 ALD Temperature Cycling for Uniform Infilling of Macroscopic Nanoporous Solids*, Benjamin Greenberg,*** *K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Uniform ALD infilling of macroscopic nanoporous solids with aspect ratio greater than 10^4 can require precursor dose times on the order of 10^3 seconds, at least four orders of magnitude longer than typical dose times for ALD on wafers. For ALD processes based on relatively stable precursors and straightforward chemistries, such as ALD of Al_2O_3 from trimethylaluminum (TMA) and H_2O, very long doses are generally harmless, but for some ALD processes, precursor decomposition and other side reactions are significant concerns. For example, at a deposition temperature of 180 °C, which has been chosen previously for ZnO ALD infilling to ensure rapid removal of H_2O from nanopores during purging,[1] diethylzinc (DEZ) decomposition[2] and surface Zn deethylation[3] may be substantial on the ~10^3 s timescale.

In this work, we investigate the potential of temperature cycling as a route toward rapid yet controlled infilling of macroscopic nanoporous solids. We infill Al_2O_3 nanoparticle compacts of ~1.5 mm thickness and ~100 nm pore size (aspect ratio > 10^4) with ZnO using DEZ and H_2O as precursors, and we cycle the substrate temperature between ~160 °C (during H_2O purges) and ~120 °C (during all other steps). DEZ infiltration is accomplished via static dosing, wherein DEZ vapor is held in the ALD chamber for >10^3 seconds with the pump valve closed so that, in principle, diffusion/reaction and saturation are observable as a rise (due to byproducts) and flattening of the ALD chamber pressure, respectively. The 120/160 °C cyclical-temperature process produces clear saturation signals in the pressure trace, whereas fixed-temperature processes carried out entirely at 120 or 160 °C do not, apparently due to incomplete H_2O removal at 120 °C and DEZ decomposition and/or other side reactions at 160 °C. We use a variety of characterization techniques, including SEM/EDS, XRD, and electrical conductivity measurements, to assess the uniformity and purity of the ZnO infills.

1. A. Cendejas, D. Moher, and E. Thimsen, J. Vac. Sci. Technol. A **39**, 012406 (2021).
2. J. D. Ferguson, A. W. Weimer, and S. M. George, J. Vac. Sci. Technol. A **23**, 118 (2005).
3. T. Weckman and K. Laasonen, J. Phys. Chem. C **122**, 7685 (2018).

9:00am **AP+PS+TF-WeM-4 Plasmonic Plasma Process for Room Temperature Growth of High-quality Ultra-thin Dielectric Films*, Takeshi Kitajima,*** *M. Miyake,* National Defense Academy, Japan*; K. Watanabe,* National defense Academy, Japan*; T. Nakano,* national defense Academy, Japan

Catalytic surface reactions utilizing gold nanoparticle plasmons have been utilized in various applications in recent years.[1] We have applied hot electrons supplied from gold nanoparticles to plasma surface reactions to use them to form high-quality ultrathin dielectric films at room temperature.[2] We focused on the mixed effect of visible light for plasmon excitation and plasma VUV emission and discovered the effect of green light excitation that promotes radical nitriding. Due to the mercury probe measurement and TEM imaging, the film grown have sperior dielectric feature and uniformity with less plasma induced damage in spite of nonuniform formation of gold nanoparticles.

In the growth sequence, Au was vapor-deposited on a SiO_2 / Si (100) substrate in an ultra-high vacuum chamber with an average thickness of 0.4 nm by electron beam deposition to form Au nanoparticles (C) on the surface. A 30 mTorr N_2-inductively coupled plasma was generated in the attached chamber, and the sample was irradiated with N radicals (R) that passed through a 30 line/inch SUS304 single mesh with the configuration shown in Fig. 1 (a) for 5 minutes. A filter and a white LED controlled the wavelength of light (L), and VUV light from N_2 plasma was mixed. The reaction condition consisting of the above is RLC. Figure 1 (b) shows the dielectric characteristics of the SiON film {leakage current and EOT (equivalent oxide film thickness) when 1 V is applied}. In green light suitable for Au plasmons, the hot electrons (~ 4 eV) generated by the deexcitation of plasmons enabled the bond conversion from Si-O to Si-N the ultra-thin SiON shows the same characteristics as the ideal SiON film. By mixing VUV, it is possible to increase the film thickness further and reduce leakage.

Cross-sectional TEM image of SiON film after plasmonic process is shown in Fig. 1 (c). Beneath the Au particle SiON film with wide range of uniformity is confirmed and the single crystal lattice of Si substrate is clearly identified.

From the above, it is considered that the reaction between the adsorbed N radicals and Si proceeded, and a quality SiON film was formed by superimposing the photoelectron emission from the VUV light on the hot electron injection from the gold nanoparticles by green light irradiation.

1 C. Clavero, Nat. Photonics 8, 95 (2014).

2 T. Kitajima, M. Miyake, K. Honda, and T. Nakano, J. Appl. Phys. 127, 243302 (2020).

9:20am **AP+PS+TF-WeM-5 Time Resolved Energy Diagnostics of HiPIMS Discharges With Positive Cathode Reversal*, Zachary Jeckell,*** *T. Choi, M. Hossain, D. Kepelyan, N. Vishnoi,* University of Illinois at Urbana Champaign*; B. Jurczyk,* Starfire Industries*; D. Ruzic,* University of Illinois at Urbana Champaign

This work investigates the temporal evolution of a high-power impulse magnetron sputtering (HiPIMS), with a positive cathode reversal, discharge by using the Hiden ANALYTICAL PSM probe that can measure the ion energies as well as perform charge to mass (q/m) measurements. This work builds off other diagnostic work done on the chamber such as time resolved electron energy distribution functions from our time resolved Langmuir probe technique, previous work with measuring ion energy distribution functions using the SEMION probe, as well as preliminary measurements taken with the PSM probe. This work was performed on several different target materials such as Ag, Ti, ZnTe, and W. The diagnostic capabilities of the PSM allows for differentiation between the working gas and target material ions which enables us to calculate the ratio of target ions for a given condition. Previous work we have done has shown that at early stages of the positive cathode reversal there is an elevated population of metal ions and that the overall fraction of metal to working gas fraction is at its highest. Time and energy resolved mass spec data was collected on this system for a variety of conditions such as pulse lengths, pressures, and target material with the objective of developing a better understanding for the energetics at play. Additionally, by running the PSM with the filament on and a properly set repelling voltage it was possible to get a sense of the neutral energies as well. This required a deconvolution of the energy that the neutrals gain from the ionization from the filament. The goal was to use the results of those experiments to build a framework of understanding and to use that information to deposit better films, such as increasing the hardness of TiN, reducing the resistivity of N doped ZnTe, improving the crystallinity of W films or improving the optical properties of a Ag thin film.

9:40am **AP+PS+TF-WeM-6 Electron-Enhanced ALD of TiO_2, TiN, and TiCN at Low Temperature Using TDMAT Together with O_2 and NH_3 Reactive Background Gas***, Z. Sobell, A. Cavanagh,* ***Steven George,*** University of Colorado Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiO_2, TiN, and TiCN films at T < 70 °C.Three Ti-based films were grown using sequential exposures of tetrakis(dimethylamido) titanium (TDMAT) precursor and electrons together with a continuous reactive background gas (RBG) (Figure 1). The electrons accelerated across a grid bias of 100 V desorb surface species by electron stimulated desorption.The electrons also dissociate the RBG as they travel to the substrate.The RBGs utilized to tune the film composition were oxygen (O_2) for TiO_2 and ammonia (NH_3) for TiN and TiCN.

TiO_2 EE-ALD was performed at T < 70 °C using TDMAT together with an O_2 RBG at ~1 mTorr. O_2 is believed to be dissociated by the electron beam, creating O radicals that add oxygen to form TiO_2 and remove N and C from the TDMAT precursor. XPS showed no detectable C or N in the TiO_2 films and a slightly O-rich stoichiometry. Oxygen-rich TiO_2 films may be more photochemically active due to bandgap narrowing and could be useful in photocatalysis.

TiN EE-ALD was conducted at T < 70°C using TDMAT together with an NH_3 RBG at a pressure of ~1 mTorr. NH_3 is believed to be dissociated by the electron beam, liberating H and NH_x radicals that facilitate Ti nitridation and C removal from the film. Electron exposures for 20 seconds led to the rapid nucleation of TiN films with purities of > 96% and ultralow resistivities of < 120 μΩ-cm. These films may be useful as diffusion barriers in backend interconnects.

Incomplete C removal resulted from shorter electron exposures during TiN EE-ALD using TDMAT with NH_3 RBG.This carbon residual provides a pathway for the deposition of TiCN, an important amorphous ternary nitride diffusion barrier.TiCN EE-ALD film growth and properties were explored for electron exposure lengths from 20 seconds to 0.5 seconds.Shorter electron exposures led to an increase of the C:Ti ratio from ~0.03 to ~0.33 as measured by x-ray photoelectron spectroscopy (XPS) (Figure 2).Shorter electron exposures also produced a decrease in film density from ~5.3 g/cm^3 to ~3.3 g/cm^3.In addition, shorter electron exposures yielded an increase in the film resistivity from < 120 μΩ-cm to ~2000 μΩ-cm as measured by ex situ spectroscopic ellipsometry (SE).Consequently, the enhanced diffusion barrier properties of TiCN EE-ALD films will be accompanied by higher film resistivities and lower film densities than TiN EE-ALD films.

11:00am **AP+PS+TF-WeM-10 A Non-Violent Approach to Remove SiN:H Surface Impurities (HCl) at Room Temperature***,* ***Tsung-Hsuan Yang,*** *T. Wang, G. Hwang,* University of Texas at Austin*; P. Ventzek, J. Zhao,* Tokyo Electron America, Inc.

Our research presents a non-violent approach to remove H^+/Cl^- pairs, a common reaction byproduct, after depositing chlorosilane-type Si precursors (such as dichlorosilane, SiH_2Cl_2) on a SiN surface. While previous studies have suggested the use of H radicals in NH_3 and CH_3NH_2 plasma to remove Cl impurities, these methods have limitations in high-aspect-ratio structures. The recombination rate of radicals may be too fast to reach the bottom of the trench, resulting in the accumulation of Cl and possibly the formation of a salt layer that inhibits further film growth. Through first-principles calculations, we propose an alternative solution by introducing polar molecules, such as NH_3, N_2H_4, CH_3NH_2, and $(CH_3)_2NH$. When these polar molecules are dosed onto the surface, they can first abstract the H^+ from the H^+/Cl^- pair to form a complex with Cl^-. Adjacent polar molecules then solvate the complex, forming a stable "microsolvation cluster." This cluster effectively captures Cl^- while weakening the interactions between Cl^- and surface amine groups, providing a pathway for HCl desorption with a lower energy barrier. Our calculations of free energy surface show that when the surface is saturated with CH_3NH_2 molecules, the energy barrier for HCl desorption can be significantly reduced at 300K. Based on these promising findings, we propose a novel and non-aggressive atomic layer deposition (ALD) scheme to grow SiN at low temperatures while achieving a higher growth rate.

11:20am **AP+PS+TF-WeM-11 Influence of Plasma Species on the Growth Kinetics and Properties of Epitaxial InN Films Grown by Plasma-Enhanced Atomic Layer Deposition***,* ***Jeffrey Woodward,*** *D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Huntington Ingalls Industries*; S. Walton,* U.S. Naval Research Laboratory*; S. Rosenberg,* Lockheed Martin Space Advanced Technology Center*; J. Hite, M. Mastro,* U.S. Naval Research Laboratory

The controlled co-delivery of reactive and energetic plasma species during plasma-enhanced atomic layer deposition (PEALD) enables the growth of epitaxial layers at significantly reduced temperatures which are prohibitive to other methods. However, this capability is challenged by the complexity which arises from the reliance on plasma-surface interactions, and it is thus necessary to understand the influence of the plasma properties on the growth kinetics and resultant film properties. Among the III-nitride binary compounds, indium nitride (InN) is particularly well-suited for the investigation of the roles of reactive and energetic plasma species, as high-quality crystalline films can be achieved using trimethylindium (TMI) and a relatively simple N_2/Ar plasma rather than N_2/Ar/H_2 or NH_3/Ar plasmas which generate greater varieties of species. This was explored in recent studies of InN PEALD on gallium nitride (GaN) using *in situ* synchrotron x-ray scattering, which revealed that the growth mode is correlated with the relative density of atomic N, while coarsening behavior is influenced by ion flux.[1]

In this work, epitaxial InN films are grown by PEALD on GaN (0001) at approximately 320 °C using TMI and N_2/Ar plasma within various regimes of plasma species generation in order to investigate the influence on the resultant film properties. Optical emission spectroscopy and Langmuir probe measurements are used to correlate the production of atomic N and ions with the N_2 and Ar gas flows into the inductively coupled plasma (ICP) source. The InN films are characterized by atomic force microscopy (AFM), x-ray reflectivity (XRR), high-resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), synchrotron grazing incidence wide-angle x-ray scattering (GIWAXS), and x-ray photoelectron spectroscopy (XPS). The films are found to exhibit wurtzite phase and sixfold rotational symmetry with a clear epitaxial relationship to the GaN. Low fluxes of atomic N are found to promote larger domains, increased crystalline order, and smoother morphology compared to films grown with high atomic N fluxes. For the high atomic N flux condition, increasing ion flux is found to promote a very rough morphology containing large cluster-like features and decreased in-plane crystalline order, but increased out-of-plane crystalline order and a reduction in mosaic twist.

[1] J. M. Woodward *et al*., J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:40am **AP+PS+TF-WeM-12 One Step Synthesis of Patterned Coatings Using Immobilized Filaments in an Atmospheric Pressure Dielectric Barrier Discharge. Effect of Gap and Power Pulsing.***, M. Brabant,* ***Annaëlle Demaude,*** *D. Petitjean,* Université Libre de Bruxelles, Belgium*; K. Baert, T. Hauffman,* Vrije Universiteit Brussel, Belgium*; M. Gordon,* University of California Santa Barbara*; F. Reniers,* Université Libre de Bruxelles, Belgium

Deposition of patterned coatings to generate hybrid surface properties often require a multi-step process, such as the use of masks or lithography [1]. We proposed recently a simple scalable method for the deposition of patterned coatings (morphological and chemical contrasts) [2]. As a case study, the deposition of propargyl methacrylate (PMA) based-coatings was realized, as, due to its structure (one double and one triple bond), this molecule allows very fast deposition, and can lead to hydrophobic coatings, without the need of fluorinated atoms. Moreover, we showed that, depending on the deposition conditions, one could obtain hybrid hydrophilic/hydrophobic patterns.

To test the flexibility and the limits of the method, we now investigate further this route and try to understand better the effects of the gap between the electrodes and of the pulsed/non pulsed injection of the power. The deposited coating was characterized using μ-XPS, FTIR and contact angle measurements, whereas the discharge was characterized using a high intensity camera, electrical measurements (oscilloscope and Rogowski coil), and mass spectrometry. Due to the DBD configuration, the coating exhibits two distinct areas : the spot (S) area, corresponding to the coating deposited under the filament position, and the between spot (BS) area, corresponding to the coating deposited outside the filament position.

Filaments are immobilized thanks to beads fixed to one of the dielectrics, reducing locally the gap and therefore igniting specifically the discharge at these locations. Here the gap was fixed at 2, 2.5 and 3 mm. it is shown (using a high intensity camera, and electrical measurements) that an increase in gap leads to more energetic discharges inside the filaments. As shown by XPS, this leads to a lower preservation of the precursor structure for the "S"area coating. In parallel, due to higher voltages needed to light up the discharge, surface discharges take place between the filaments leading to subsequent deposition also between the spots located under the filaments.

Pulsing the power (in the ms range) leads to more localized filaments, to a global change in the plasma behavior and to a change in the coating chemistry [3] .

References :

[1]. A. Demaude *et al*., *Langmuir*, 2019, *35* (30), 9677–9683

[2] A. Demaude *et al*., *Advanced Science*. 2022, *9* (15), 2200237

[3] A. Demaude *et al*., *Plasma Chemistry and Plasma Processing*, submitted.

12:00pm **AP+PS+TF-WeM-13 Effect of Bias Pulsed Plasma Enhanced Atomic Layer Deposition for Void-Free SiO_2 Gap-Fill of High Aspect Ratio Trench Structures***, **Ye Ji Shin,** H. Kim, G. Yeom,* Sungkyunkwan University, Korea

In 3-dimentional (3D) device structures, cells are getting thinner and higher to increase the density of devices which resulted in High Aspect Ratio (HAR) structures. Gap-fill process is one of the processes that could affect the device performance of HAR trench structures. Void and seam are observed after the gap-fill process and they allow penetration of the chemical etchant used in subsequent processes, and which degrades isolation performance and increases leakage currents. To solve this issue, various processes such as thermal ALD processes with inhibitors, plasma enhanced ALD with substrate biasing, etc. have been used but, with increasing the aspect ratio of the structure, it is found to be difficult to fill the gap completely without void or seam in the trench. In this study, bias power with pulsing was introduced to PEALD processes for void and seam free SiO_2 gap-filling. Pulsed bias power with various pulse duty ratio from 30 to 75% were used and compared with continuous wave (CW) bias power and no bias power to identify the effect of bias pulsing. The results showed that, as the bias pulse duty ratio was decreased, void and seam were decreased and disappeared at HAR trench structures even with negative bowing. The pulse biasing with low duty ratio appeared to open the opening of the trench top while the pulse biasing with high duty ratio and CW biasing operation appeared to close the opening of the trench top possibly due to differences in combined effect of ion bombardment flux and deposition. Eventually, void-free SiO_2 gap-fill for HAR trench structures were obtained with bottom-up filling under the pulsed bias conditions. Detailed experimental results and analysis data will be shown in the presentation.

Thin Film Division
Room A105 - Session TF2+AP+SE+SS-WeM

Controlling Microstructure and Accessing Non-Equilibrium Phases in Thin Films

Moderators: Robert Grubbs, IMEC Belgium, **Richard Vanfleet**, Brigham Young University

11:00am **TF2+AP+SE+SS-WeM-10 Stabilizing Polar Polymorphs of Scandium Ferrite for Photovoltaics***, M. Frye, **Lauren Garten,*** Georgia Institute of Technology **INVITED**

Metastability is no longer synonymous with unstable or unattainable, but further work is needed to enable the next generation of electronics and photovoltaics. In this talk I will discuss the development of a stabilization route for the P63cm phase of ScFeO3 through precursor control and interface engineering. The P63cm phase has potential for lead-free piezoelectric, photo-ferroic, and ferroelectric applications. Unfortunately, this phase is in competition with four other known polymorphs that are similar in structure and energy and there is not a well matched epitaxial substrate. So we took a different approach by controlling the atomic layering of the precursor structure and the deposition timing to stabilize the P63cm phase under conditions that previously lead to the ground state. The film structure is verified by transmission electronic microscopy and x-ray diffraction. Ab initio calculations confirm that layered growth stabilizes the metastable phase and highlights the importance of the variable oxidation state of iron, the high activation energy against diffusion, and the surface termination of the substrate in designing a stabilization approach. This work highlights routes to access similar polymorphs on an array of different substrates, opening up new materials and new device architectures.

11:40am **TF2+AP+SE+SS-WeM-12 The Role of Thermal Vibrational Disorder in the Structural Phase Transition of VO_2 Probed by Raman Spectroscopy***, **Aminat Oyiza Suleiman,*** Institut National de la Recherche Scientifique, Canada*; S. Mansouri,* Institut National del a Recherche Scientifique, Canada*; N. Émond,* Massachusetts Institute of Technology, Canada*; T. Bégin, J. Margot,* Université de Montréal, Canada*; C. Mohamed,* National de la Recherche Scientifique, Canada

Vanadium dioxide (VO_2) is a typical correlated electron material which exhibits a first-order metal–insulator transition (MIT) at a near-room temperature of about 340 K. Upon heating, VO_2 switches from an insulating monoclinic phase (M1 or M2) to a metallic tetragonal rutile phase (R). The mechanism behind the MIT in VO_2 is still controversial: Is it a structure driven Peierls transition mechanism or a Mott transition where strong electron-electron correlations drive charge localization and collapse the lattice symmetry? By directly comparing the electrical and lattice–dynamic properties of VO_2, useful information about the MIT/SPT in VO_2 can be obtained.

Herein, we therefore present a detailed Raman study of undoped (M1) and Cr-doped (M2) VO2 thin films as a function of temperature. The studied VO_2 films with different thicknesses are deposited on c- and r-sapphire substrates. While their structural properties and morphology are examined by XRD and AFM techniques, respectively, Raman measurements are correlated to four-point probe resistivity measurements, giving an insight into the coupling between VO_2 structural phase (SP) and MI transitions. By distinctively combining the Raman data with information from reported EXAFS data, a relationship between the Raman intensities and the mean Debye-Waller factors (σ^2: the mean-square relative displacements) is established. The temperature dependence of the vanadium dimers Waller factor (σ_R^2 (V-V)), as calculated from the Raman intensity, was found to follow the temperature profile of the σ_{EXAFS}^2 (V-V) obtained from the reported EXAFS data. These findings provide an evidence on the critical role of the thermal vibrational disorder in VO_2 phase transitions, demonstrating that by correlating Raman data with EXAFS analysis, both lattice and electronic structural dynamics can be probed.

12:00pm **TF2+AP+SE+SS-WeM-13 Interplay of Lattice Distortion and Electronic Structure in Metastable Brookite TiO_2***, **Pritha Biswas,*** Oregon State University*; M. Choi, K. Koirala, M. Bowden, L. Strange,* Pacific Northwest National Laboratory*; H. Zhou,* Argonne National Laboratory*; J. Tate,* Oregon State University*; Y. Du, T. Kaspar, D. Li, P. Sushko,* Pacific Northwest National Laboratory

Controlling the coupling between lattice distortions and electronic properties is one of the promising routes toward enhancing the performance of materials used in energy technologies, such as photocatalysis, photovoltaics, and energy storage. Oxide semiconductors that exhibit polymorphism represent a convenient class of systems to study this coupling by investigating the effect of external stimuli on transition pathways between polymorphs. Among the oxide semiconductors, earth-abundant TiO_2 exists in several polymorphic forms, including rutile, anatase, and brookite, with distinctly different structural symmetries. Compared to the common rutile and anatase polymorphs, metastable brookite TiO_2 is the least studied one due to the difficulties associated with its synthesis in a phase pure form. At the same time, mechanisms of its transformation to the more stable anatase and rutile polymorphs are promising to provide a rich insight into the relationships between the character of the lattice deformations, defect content, and electronic structure. We have developed a recipe for phase selective TiO_2 polymorph formation, where tuning of oxygen vacancy concentration drives the crystallization of amorphous TiO_2 thin films towards a specific polymorphic structure. In this study, thermal treatment was used to control the evolution of as-deposited, sputtered amorphous TiO_2 thin films towards the brookite lattice. The crystallinity and phase purity of the resulting structures were investigated by lab-based grazing incidence XRD, synchrotron XRD, and transmission electron microscopy. The dependence of structural variations present in the sample on the details of the annealing treatments was evaluated using Rietveld refinement analysis. X-ray photoelectron spectroscopy (XPS), confocal Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM) were used to understand the effect of local deformation on the electronic structure of brookite. We found a correlation between the degree of lattice parameter deviation, shifts of the Raman vibrational modes, and the position of the brookite valence band. The effect of these lattice distortions at the atomic scale on the photocatalytic activity of brookite will be discussed.

Manufacturing Science and Technology Group
Room C120-122 - Session MS+AP+AS+TF-ThA

Machine Learning for Microelectronics Manufacturing Process Control

Moderator: Tina Kaarsberg, U.S. Department of Energy, Advanced Manufacturing Office

2:20pm **MS+AP+AS+TF-ThA-1 Human-Machine Collaboration for Improving Semiconductor Process Development***, **Keren Kanarik**,* LAM Research **INVITED**

Although chips have been designed by computers for decades, the processes used to manufacture those chips are mostly developed manually – a costly endeavor using highly trained process engineers searching for a combination of tool parameters that produces an acceptable result on the silicon wafer. To assess whether AI could be beneficial in accelerating process engineering innovation and reducing costs, humans and machine algorithms were benchmarked on a virtual high aspect ratio plasma etch process [Kanarik, et al. Nature 616, 707–711 (2023)]. This talk will review results and take a behind-the-scenes look at the study, which showed a “human first, computer last” approach could reach process engineering targets dramatically faster and at half the cost compared to today's approach. While human expertise and domain knowledge are essential for the foreseeable future, the results point us to a path to foundationally change the way processes are developed for manufacturing chips.

3:00pm **MS+AP+AS+TF-ThA-3 Machine Learning-based Atomic Layer Deposition***, **Kanad Basu**,* University of Texas at Dallas **INVITED**

Atomic Layer Deposition (ALD) is dependent on a host of process parameters. These independent parameters can be set to a particular value to create customized recipes for growing films. Although they are considered to significantly influence the ALD process, existing research does not provide a methodology to quantify the impact of these parameters on growth rate and final thickness of a film. Moreover, process parameter-based thickness estimation is a resource- and time-intensive approach, requiring numerous experiments. To address these challenges, we propose a machine learning (ML)-aware strategy that generates "feature importance maps" to determine the most critical process parameters. In our study, we utilize a Veeco® Fiji Gen2 ALD system to grow a CeO_2 film. Specifically, our study is associated with 78 process parameters, which include chuck temperatures, chamber temperatures, line temperatures, precursor temperatures, gas flow rates, among others. Our approach utilizes a random forest classifier, which is identifies the top-10 features (parameters) that affect ALD processes. The proposed approach furnishes promising results of up to 99% thickness prediction accuracy using the deduced top-10 features. These results are subsequently validated using in-situ spectroscopic ellipsometry, thereby advocating its effectiveness in generating the feature importance maps. We posit that only these ten features can be utilized to monitor and control ALD processes. Furthermore, in this analysis, we demonstrate the robustness of our solution, which is independent of the type of ALD process considered - standard ALD process or temperature-dependent Temperature-Time-Thickness (TTT) ALD processes. Moreover, by monitoring just ten of the 78 process parameters, the proposed approach has implications of reduced data dimensionality (up to 87.2% reduction in feature space).

3:40pm **MS+AP+AS+TF-ThA-5 Rapid Optimization of Gap-Fill Recipes Using Machine Learning***, **Sebastian Naranjo**, L. Medina de Oliveira, M. Chopra,* Sandbox Semiconductor

Creating and optimizing deposition recipes for nanostructured devices is costly and time-consuming. A major source of defects and device performance degradation is the formation of interior voids. These voids can have a number of causes, including non-uniform deposition rates along the substrate surface due to imperfect seeding and/or mass transport and reaction kinetics factors, as well as critical dimension variations in the initial profile due to imperfections in preceding processing steps. For example, during electroplating, the substrate surface is seeded before material deposition is set to fill the gap. Non-conformal seedings can cause the deposited material to accumulate at different rates and lead to localized voids. Void defects can also occur in highly conformal processes such as atomic layer deposition or chemical vapor deposition due to critical dimension variations such as bowing or tapering in the pre-deposition profile. Current methods for optimizing process performance rely largely on trial and error. Here we present a cost-effective and systematic computational approach to optimize recipe conditions using Sandbox Studio AI, which employs a combination of feature scale modeling and machine learning to rapidly predict process outcomes for a given electroplating system using a minimal number of experiments. In this approach, we first use critical dimension information about the fill height and void defects from a set of experiments to calibrate a feature scale model. We then use the calibrated model to predict critical dimension outcomes for thousands of possible process parameter combinations. These predictions are used to maximize process window stability and provide recipe recommendations that minimize the formation of voids even in the presence of seeding or initial profile imperfections. The showcased approach demonstrates how computational modeling can be used to accelerate learning cycles, improve process quality, and reduce development costs.

Manufacturing Science and Technology Group
Room Oregon Ballroom 203-204 - Session MS-ThP

Manufacturing Science and Technology Poster Session

MS-ThP-1 Autonomous Synthesis in the MBE Using Real-Time Artificial Intelligence*, **Tiffany Kaspar**, L. Wang, J. Christudasjustus, M. Sassi, B. Helfrecht, J. Pope, A. Harilal, S. Akers, S. Spurgeon,* Pacific Northwest National Laboratory

Materials are the key components of nearly all advanced technologies, including quantum information systems, microelectronics, catalysis, and energy conversion and storage. Modern synthesis methods enable the fabrication of an ever-expanding array of novel, non-equilibrium, and/or metastable materials and composites that may possess unique and desirable functionality. Thin film deposition by molecular beam epitaxy (MBE) can produce atomically precise (or nearly so) materials with a wide range of functional electronic, magnetic, ferroelectric/multiferroic, optical, and/or ion-conducting properties. The current state of the art in precision design of functional materials is to manually explore the "growth phase space" of the deposition techniqueto optimize the film properties of interest. Limitations of time and resources often result in incomplete exploration of the growth phase space and resulting properties. Faced with this lack of complete information, materials design and synthesis decisions are made based in part on intuition and luck, slowing both materials optimization and materials discovery.This current synthesis paradigm can be disrupted by employing artificial intelligence (AI)-accelerated analysis of *in situ* and *ex situ* data streams that will enable targeted synthesis of novel materials with desired structure, chemical stability, and functional properties.Here we present a preliminary implementation of such an AI-controlled MBE.We are integrating the control of key synthesis parameters (temperatures, gas flow rates, shutters) with AI-guided computer control.Guidance will be based on near-real-time analysis of reflection high energy electron diffraction (RHEED) patterns using sparse data analytics, with low-latency feedback to the control software.As an initial demonstration, we will control the morphology and phase purity of epitaxial anatase TiO_2 thin films.

MS-ThP-2 Machine Learning Based Virtual Metrology for Effective Process Control in High Product Mix Manufacturing*, **Hyung Joo Lee**, S. Choi,* Siemens EDA, Republic of Korea*; N. Greeneltch, S. Jayaram,* Siemens EDA

1. Introduction

The semiconductor foundry industry faces challenges with high product mix manufacturing, requiring increased flexibility in managing diverse customer demands. Coordinating multiple chambers and process steps with different designs and technology nodes is complex, resulting in reduced yields and increased costs.

2. CVD Process Challenges

The CVD process in semiconductor manufacturing experiences thickness variations due to device layout design and chamber condition drift. Lack of control across layouts affects transistor parameters and yield. Managing chamber-by-chamber variations is crucial for high-volume manufacturing, but current solutions hinder fab line management and throughput.

3. VM Approach and Modeling

Virtual metrology (VM) addresses the trade-off between metrology activities and cost by utilizing data from the process chamber (FDC) to predict metrology results. Design features are extracted and used for prediction across layouts and technologies, benefiting new layouts and production stages. Siemens' Calibre® software is employed for feature extraction, and ML methodologies construct the VM model. Results demonstrate the superiority of the VM model with design features and FDC.

4. APC System and Results

An APC system using the VM model for R2R control is proposed. It incorporates design features, FDC, and measurements to achieve the desired thickness target. The system triggers updates to the VM model based on prediction errors. The APC system significantly improves process capability and reduces film thickness variations. Control simulation confirms the effectiveness of the APC system in a high-mix product foundry fab setting.

5. Summary

The semiconductor foundry industry faces challenges in high product mix manufacturing. The CVD process experiences thickness variations from design features and chamber conditions, impacting yield. A VM approach, incorporating design features and FDC, improves process control. An APC system based on the VM model further enhances thickness control, demonstrating significant improvements in process capability and thickness variation reduction.

MS-ThP-3 Experimental 3D Maintenance Work Measurement and Analysis for Maintenance Improvement and Enhancement of Productivity of Semiconductor Manufacturing Equipment*, **Takashi Numata**, Y. Ogi, K. Mitani, R. Kawamata, N. Ikeda, T. Ege,* Hitachi, Ltd., Japan*; Y. Kadomoto, R. Ishibashi, Y. Shengnan, Y. Sakka, Y. Nakamura, K. Sato,* Hitachi High-Tech Corporation, Japan

Recently, high machine availability of semiconductor manufacturing equipment has become more important, and shortage of field service engineers has become serious. Therefore, maintenance improvement which enable to increase the capacity with inexperienced field engineers and realize productivity improvement of semiconductor manufacturing equipment has been needed.

Based on these circumstances, we have proposed maintenance work measurement and analysis technologies for maintenance improvement of semiconductor manufacturing equipment. Our targets are to reduce durations of and maintenance work, and a rate of reclean (failure of maintenance) especially focusing on periodical maintenance. Maintenance work measurement and analysis have a potential to enable us to extract work differences between skilled and unskilled maintenance workers, extract complex and difficult characteristics of maintenance work, and support and/or reduce such complex and difficult maintenance work.

In this study, we developed a measurement system with 3D sensors and motion sensors, experimentally measured maintenance work of semiconductor manufacturing equipment such as parts assembly and wiping by using the developed system, and extracted indicators of personal differences among workers. We extracted various indicators including task time, working posture, amount of head motion, change of eyesight, amount of hand motion. As a result, we demonstrated representative differences of extracted indicators between an experienced maintenance worker and an inexperienced maintenance worker.

From the result, it was suggested that application of maintenance work measurement and analysis system with results of maintenance enable us to extract important factors to cause reclean, and standardize maintenance work based on skilled workers' movements and/or successful works. Then effective countermeasures for support and/or reduction of difficult task will be applied based on the results of maintenance work analysis.

Atomic Scale Processing Mini-Symposium
Room C124 - Session AP+PS-FrM

Atomic Scale Processing Late Breaking Atomic Layer Etching and Area Selective Deposition

Moderator: Eric Joseph, IBM T.J. Watson Research Center

8:20am **AP+PS-FrM-1 Atomic Layer Etching of SiO_2 via H_2/SF_6 Plasma and TMA**, ***David Catherall,*** *A. Minnich,* California Institute of Technology

The quality factor of ultrahigh Q silica microdisk resonators has reached values exceeding one billion but remains at around an order of magnitude below intrinsic upper limits due to surface-roughness scattering. Atomic layer etching (ALE) has potential to mitigate this scattering because of its ability to smooth surfaces to sub-nanometer length scales. Here, we report an ALE process for etching of SiO_2 using sequential exposures of TMA and $Ar/H_2/SF_6$ plasma. The $Ar/H_2/SF_6$ plasma has been reported to enable in-situ production of HF, enabling HF exposures in the ALE process without the need for an external source of HF vapor. We observe etch rates up to 0.6 Å per cycle and examine the effect on surface roughness. This work advances a process of relevance to ultrahigh Q silica resonators which are fundamental elements of on-chip photonic devices such as frequency combs.

8:40am **AP+PS-FrM-2 Area Selective Deposition of HfO2 on Oxide and Nitride Surfaces**, ***ByungChan Lee,*** Incheon National University, Republic of Korea; *C. Nguyen,* Incheon National University, Viet Nam; *S. Shim, Y. Kang, H. Lee,* Incheon National University, Republic of Korea

Due to the scaling down in the Si device fabrication, the aspect ratio and complexity of 3D device structures is rapidly increased, leading to the limitation of the conventional fabrication process including deposition, etching, lithography and so on. Area selective deposition (ASD) has received great attentions from the Si industry as one of the unit processes to overcome the limitations. ASD is developed based on the atomic layer deposition (ALD) which has the unique self-saturation surface reaction mechanism. The surface chemical properties are modified by using the promoter or inhibitor which promotes or inhibits the thin film growth, respectively. Accordingly, the ALD thin films are selectively deposited on the desired area. At the beginning of the ASD research, the self-assembled monolayers (SAMs) were commonly used as an inhibitor. But the inherent size of SAMs has potential problems for the pattern interference in nm-size scale. In this study, we investigated the ASD using a small molecule inhibitor (SMI). We selected the aldehyde molecules as SMI to inhibit the nitride surface but not on oxide surface. By using density functional theory (DFT) calculation, adsorption behaviors and energetics of the aldehydes was studied on nitride and oxide surfaces. From the experiments, it was observed that the aldehyde selectively adsorbs on only nitride surface but not on oxide surface and block the HfO_2 deposition until 15 cycles. The inhibition of nitride surface using SMI can contribute to many unit processes of Si device fabrication by simplifying the process scheme.

9:00am **AP+PS-FrM-3 Surface Functionalization of SiN_x over SiO_2 with Aldehydes to Enable Area-Selective Atomic Layer Deposition**, ***Andrew Kaye,*** Colorado School of Mines, USA; *S. Agarwal,* Colorado School of Mines; *B. Zope, A. Derecskei, R. Pearlstein, X. Lei,* EMD Electronics, USA

As the semiconductor device dimensions continue to shrink, area-selective atomic layer deposition (AS-ALD), which is a bottom-up technique, can address the challenges associated with device fabrication. SiO_2 and SiN_x are two of the most commonly used dielectrics in semiconductor devices, and deposition on one dielectric with minimal deposition on the other can simplify processing. For example, in 3D-NAND structures, there are alternating layers of SiO_2 and SiN_x, and during processing, it is desirable to grow a metal oxide on SiO_2 with no growth on SiN_x. In AS-ALD, inhibitor molecules can be used to functionalize SiN_x because very few ALD precursors have an inherent binding selectivity to SiO_2 over SiN_x. Finding inhibitor molecules that selectively adsorb on SiN_x over SiO_2 is also challenging since on SiO_2 films contain SiOH groups, which react readily with many compounds such as chlorosilanes, alkoxides, and aminosilanes. We have previously shown that aldehydes selectively adsorb on SiN_x with minimal adsorption on SiO_2.

This work focuses on the adsorption mechanisms of two aldehydes, 3,5,5-trimethylhexanal (TMH) and dodecanal (DDA), on plasma-deposited SiN_x films characterized with *in situ* attenuated total reflection Fourier transform infrared spectroscopy. We show that TMH adsorbs on SiN_x forming silyl ethers, amino alcohols, enamines, and imines with surface $-SiH_x$ and $-NH_x$ groups being the reactive sites. Reaction of DDA with SiN_x leads to the formation of similar surface species except for enamines. Amino alcohols are reaction intermediates formed due to the reaction of surface amines with aldehydes — the complete reaction should result in the formation of imines with H_2O as the byproduct. The presence of amino alcohols is not desirable since the -OH group may react with metal ALD precursors and reduce selectivity. We show that once the amino alcohols are formed on the surface, they cannot be converted to imines by increasing the substrate temperature. The surface composition of the underlying SiN_x film greatly affects the uptake of the aldehyde and the relative ratio of the surface species formed after adsorption of both aldehydes. The aldehydes desorb from the surface when the substrate temperature is increased, and further desorption occurs over time at elevated temperatures. After desorption at a constant temperature, TMH can be replenished by redosing. In practical applications the SiN_x surface is partially oxidized upon exposure to the atmosphere. To understand the effect of surface oxidation, the plasma-deposited SiN_x films were exposed to the atmosphere for several days. The atmosphere exposed SiN_xfilms were then cleaned with D_2 plasma to possibly etch the surface oxide layer to enhance reactivity by restoring $-SiD_x$ and $-ND_x$ surface species.

9:20am **AP+PS-FrM-4 Surface Reactions During Atomic Layer Etching of Platinum by High-Density Nitrogen-Oxygen Plasma and Organic Acid Vapor**, ***Thi-Thuy-Nga Nguyen,*** Nagoya University, Japan; *D. Akagi, T. Uno, T. Okato,* AGC Inc., Japan; *K. Ishikawa, M. Hori,* Nagoya University, Japan

Anisotropic patterning process of metal layers in complex nanostructures is a big challenge. Pt is a promising material, but it is a hard-to-etch material. Dry etching of Pt thin film has been developed by using halogen-based plasmas of SF_6, CF_4, or Cl_2 gas. However, the anisotropic etch profiles of Pt films in most cases have not achieved due to the redeposition of the etch residues that produces fences or tapered sidewall. Recently, non-halogen chemistry for noble metal etching has been developed using atomic layer etching (ALE) with surface modification by oxidation and removal of the oxide layer by vapor of organic compounds [1].

Our developed floating wire-assisted high-density plasma at medium pressure significantly increases the chemical reaction rate to the sample surface, that was applied in the reduction of SnO_2 [2] and dry etching of TiAlC [3]. Here, we have demonstrated ALE of Pt via high-density plasma oxidation and removal of the modified layer by organic acid vapor or organic acid plasma. High-density nitrogen-oxygen based plasma (N-O plasma) was generated to fully oxidize Pt surface and form a dominant oxidation state (Pt^{4+}). Surface modifications after the reactions of Pt with N-O plasmas and the modified layer with organic acid vapor or plasma were analyzed by X-ray photoelectron spectroscopy. The film thickness was characterized by ellipsometry and X-ray reflectivity. Surface roughness was analyzed by atomic force microscopy, and patterning profiles were observed by transmission electron microscopy. The N-O plasmas and organic acid plasmas were diagnosed by high-resolution optical emission spectroscopy.

The formation and desorption of organometallic compounds on Pt surface are able to be atomic-level controlled at low temperature (less than 100 °C). A smooth surface of Pt film was obtained with the etch depth per cycle from 0.3 to 0.7 nm/cycle. The exposure of Pt film to N-O plasmas determines the dominant oxidation state, surface roughness, and thickness of the modified layers, that strongly affects to etching performance of Pt film. The non-halogen atomic layer etching of Pt has been successfully developed in this study.

[1] J. Chang and J.P. Chang, J. Phys. D: Appl. Phys.50, 25 (2017).

[2] T.T.N. Nguyen et al., Plasma Process. Polym. 19, 6 (2022).

[3] T.T.N. Nguyen et al., Sci. Rep. 12, 1 (2022).

9:40am **AP+PS-FrM-5 Isotropic Plasma-Thermal Atomic Layer Etching and in-Situ Atomic Layer Deposition Passivation of Aluminum Films for Superconducting Quantum Devices**, ***Haozhe Wang,*** Duke University; *I. Chen, D. Catherall, A. Hossain, A. Minnich,* California Institute of Technology

Metallic and dielectric film surface imperfections negatively impact the performance of superconducting quantum devices, including qubits and microwave kinetic inductance detectors. Despite considerable exploration into the effects of these imperfections on decoherence and low-frequency fluctuations, contemporary microfabrication methodologies fall short in rectifying them. Here, we report an atomic layer etching and in-situ deposition (ALE/ALD) process that enables the etching of the native oxide and passivation of aluminum films, all in high vacuum. The process for both ALE and ALD involves sequential exposures to SF_6 plasma and TMA at temperatures around 300 °C; whether the exposures lead to deposition or etching is controlled by adjusting the duration of each dose at the selected temperature. The resulting films are characterized using x-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, and energy-dispersive spectroscopy. The characterization methods indicate that the ~ 40 Å thick native oxide was removed and the resulting surface passivated with ~ 10 Å of AlF_3. Using x-ray photoelectron spectroscopy, we confirmed that the films are resistant to re-oxidation after exposure to the atmosphere for nine months. Our approach to engineer the surfaces of superconducting films at the atomic scale may enable superconducting quantum devices with improved performance.

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