Monday Afternoon, June 29, 2020

Atomic Layer Etching
Room Baekeland - Session ALE1-MoA

ALE of Metals and Alloys

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), Alfredo Mameli, TNO/Holst Center

1:30pm **ALE1-MoA-1 Mechanistic Insights into Thermal Dry Atomic Layer Etching of Metals and Alloys*, Andrew Teplyakov,*** University of Delaware **INVITED**

The mechanisms of thermally induced reactions of atomic layer deposition (ALD) and atomic layer etching (ALE) can be in sometimes viewed as proceeding in opposite directions. However, for atomic layer processing of metals, that would mean that the best designed and most efficient reaction pathways leading to metal deposition would produce insurmountable energy barriers for a reverse process to occur spontaneously. If ligand detachment, exchange, and decomposition could be desirable for ALD, the etching of the same metals would require careful consideration of the etching mechanisms at the atomic and molecular level. Given that the mechanisms of ALE can be very complex, the key concepts and approaches will be described here for thermal dry etching processing and for distinguishing thermodynamic and kinetic regimes of etching. The mechanistic investigation of thermal dry etching of cobalt, iron, and CoFeB alloy will be the primary target of this work. The effects of surface oxidation and chlorination will be explored as a means to kinetically control the process, and preferential etching of one of the components of the alloy will be considered. Finally, a number of potential effects of the mechanisms of dry etching on the morphology of the surfaces produced and, specifically, on the "smoothing" effect of dry etching will be discussed.

2:00pm **ALE1-MoA-3 Thermal Atomic Layer Etching of Nickel Using SO_2Cl_2 and $P(CH_3)_3$*, Jessica Murdzek,*** *S George,* University of Colorado - Boulder

Thermal atomic layer etching (ALE) is defined by sequential surface modification and volatile release reactions. Thermal metal ALE is particularly challenging because the oxidation state of the metal must be changed to match the oxidation state of the volatile metal etch product. After changing the oxidation state, the metal then needs to form a stable and volatile complex. In this work, Ni ALE is developed by first changing the Ni oxidation state by chlorination using SO_2Cl_2. Subsequently, the Ni is etched by the binding of $P(CH_3)_3$ (PMe_3) ligands that can volatilize the nickel chloride.

The logic of this approach is based on the Covalent Bond Classification (CBC) method. The key is forming metal complexes that obey the "18 electron rule" or "16 electron rule". X ligands are one-electron donors like Cl. L ligands are two-electron donors like PMe_3. According to the CBC method, Ni has 10 d-electrons and Ni complexes typically have NiX_2L_3 or NiX_2L_2 configurations to obey the "18 electron rule" or "16 electron rule". The goal for Ni ALE is then to create volatile nickel compounds that are either NiX_2L_3 or NiX_2L_2 formed by sequential SO_2Cl_2 and PMe_3 surface reactions. The proposed surface chemistry for Ni ALE (Figure 1) assumes SO_2Cl_2 exposure leads to $NiCl_2$ on the Ni substrate. Then the $NiCl_2$ is volatilized by binding with PMe_3 to form either $NiCl_2(PMe_3)_3$ or $NiCl_2(PMe_3)_2$.

To demonstrate this approach, Ni ALE was studied using in situ quartz crystal microbalance (QCM) and ex situ X-ray reflectivity (XRR) measurements. The in situ QCM measurements at 200 °C revealed pronounced mass increases during chlorination with SO_2Cl_2 exposures and mass decreases during volatilization with PMe_3 exposures. The ex situ XRR measurements monitored the linear reduction in Ni thickness versus number of Ni ALE cycles. Ni etch rates were temperature dependent and varied from 0.39 Å/cycle at 125 °C to 2.16 Å/cycle at 200 °C (Figure 2). The nickel substrate was also examined versus number of Ni ALE cycles using scanning electron microscopy (SEM). The SEM images were homogeneous during the initial etching. However, there was evidence for surface pitting after 60-100 Ni ALE cycles at 150 °C.

2:30pm **ALE1-MoA-5 Thermal-Plasma ALE on Selected Metals for EUV and Integration Processes*, Xia (Gary) Sang,*** *E Chen, J Chang,* University of California Los Angeles

Nanometer-level metal patterning is receiving increasing amount of attention as they find application in back-end of line (BOEL) integration and as mask materials in Extreme Ultra-Violet (EUV) lithography. These metals are often etch-resistant, thus an effective chemical etching process needs to be developed with atomic-scale level of controllability, including uniformity and selectivity. In this talk, atomic layer etching (ALE) of Cu and Ni, for their intended application in BOEL and EUV are presented.

The unique aspect of this ALE process is the combined effect of directional chemical ions and isotropic reactive neutrals. Specifically, ALE of Ni and Cu thin film is realized using sequential surface modification by directional plasma oxidation and removal of the modified surface layer by isotropic gas phase formic acid exposure. Both blanket and patterned samples were studied using this reaction scheme. A etch rate of 3 to 5 nm/cycle is determined from the blanket samples, and final features with sidewall angle of 87 is obtained on patterned samples. The effectiveness of the approach is chemically confirmed by the measuring the increase and decrease of the signals of metal oxide peaks using XPS. Etched thickness and final feature geometry are determined by SEM and TEM.

With proper chemistries and experimental conditions, this thermal-plasma ALE is capable of delivering highly selective and anisotropic patterning of metals by creating the chemical contrast and its directionality by a reactive ion while removing the modified layer entirely with an isotropic chemical processes. Applications such as next-generation logic and spintronic memory devices could benefit greatly from this patterning approach. It is expected that the approach is generalizable to a broader selection of metals.

2:45pm **ALE1-MoA-6 Thermal-Cyclic Atomic Layer Etching of Cobalt via Organometallic Complex*, Sumiko Fujisaki,*** *Y Yamaguchi, H Kobayashi, K Shinoda, M Yamada, H Hamamura,* Hitachi, Japan*; M Izawa,* Hitachi High-Technologies, Japan **INVITED**

Isotropic atomic-layer etching (ALE), which produces atomically precise removal, will have an important role in semiconductor manufacturing. This is because highly selective ALE has become necessary to deal with processing of new materials in minitualized 3D devices. In the past several years, isotropic ALE of various materials has been reported which includes thermal ALE for metal oxides and thermal-cyclic ALE for nitride films [1]. To meet the requirements concertning the variety of materials to be etched, isotropic ALE of cobalt must be developed. Thermal ALE of cobalt has been reported by using treatment with formic acid and ligands to produce volatile cobalt complexes [2]. Also, the authors have successfully demonstrated isotropic ALE of cobalt film with smooth etched surfaces, which is important issue in the development of ALE of cobalt [3].

Experimental apparatus used in this study is 300-mm ALE tool equipped with inductively-coupled plasma source and infrared (IR) lamps. One cycle of this thermal-cyclic ALE process is roughly divided into two steps: oxidation and organometallization. In the first step, surface of cobalt film is oxidized by oxygen plasma at low temperature. In the second step, the cobalt oxide is converted into organo-cobalt complex by diketone at high temperature. The organo-cobalt complex then desorbs from the film surface because of its higher volatility. Processing condition is optimized so that the cobalt oxide layer formed in the first step is completely removed in the second step. Thus, etched amount can be controlled by oxidation thickness of cobalt and number of cyclic repetitions. Temperature cycle is important to obtain smooth etched surface. Our ALE tool produces short processing time because it is equipped with IR lamps for rapid heating. The mechanism of the surface reaction of the cobalt ALE was examined by x-ray photoelectron spectroscopy (XPS). Several oxygen 1s peaks were detected in the range from 525 to 535 eV after the first oxidation step. A peak at 530 eV decreased after the sample was exposed to diketone. This result implies that the peak at 530 eV, which is ascribed to a certain oxidation state of cobalt, dominantly contributes to formation and desorption of diketone-cobalt complex.

[1] K. Shinoda et al., J. Phys. D: Appl. Phys. **50**, 194001 (2017).

[2] C. Winter, AVS 65th, PS+EM+TF-ThM5 (2018).

[3] S. Fujisaki et al., ALE Workshop, ALE1-TuM8 (2019).

Atomic Layer Etching
Room Baekeland - Session ALE2-MoA

ALE of Metal Oxides

Moderators: Venkateswara Pallem, AirLiquide, Ishii Yohei, Hitachi High Technologies

4:15pm **ALE2-MoA-12 Ab Initio Study on the Surface Reactions of Thermal Atomic Layer Etching of Al_2O_3*, Xiao Hu,*** Chemnitz University of Technology, Germany*; J Schuster, S Schulz,* Fraunhofer Institute for Electronic Nano Systems, Germany

Thermal ALE is a novel approach for the isotropic etching of materials with atomic-level precision [1]. This technology will be important for the fabrication of advanced semiconductor devices, such as GAAFET and 3D NAND-Flash. The goal of this work was to understand the chemical mechanisms of thermal ALE using ab initio calculations. We chose Al_2O_3 ALE using HF and $Al(CH_3)_3$ as the case study. In the first half-cycle of Al_2O_3 ALE, it has been known that the fluorine precursor HF reacts with the Al_2O_3 surface to form an intermediate AlF_3 layer and H_2O molecules [1, 2]. The present work specifically focused on the second half-cycle reaction, where the metal precursor $Al(CH_3)_3$ etches the intermediate AlF_3 layer releasing volatile by-products.

Ab initio thermodynamic calculations were performed to predict the preferred etch products. Several possible Al-monomers and -dimers have been considered as the gaseous products. The calculation results show that the Al-dimers are more stable than their corresponding monomers. The most favorable etch product is the $Al_2F_2(CH_3)_4$ dimer, where two F atoms bridge the adjacent Al centers.

The surface reactions between the AlF_3 surface and $Al(CH_3)_3$ were investigated using dispersion-corrected density functional theory (DFT-D). The etch of the pristine surface by $Al(CH_3)_3$ is unfavorable due to a large reaction barrier (> 3 eV). Stability of the AlF_3 surface can be reduced by surface modification where some surface F atoms are replaced by the CH_3 groups of $Al(CH_3)_3$. This step is accomplished by a ligand-exchange reaction, as shown in Fig.1. The transition state calculated by DFT agrees well with that proposed by George et al [1].

The subsequent etch of the modified surface proceeds via two possible pathways: (1) direct etching by $Al(CH_3)_3$ with formation of Al-dimers; and (2) desorption of etch products caused by surface reconstruction. In both cases, the etch kinetics is mainly determined by the number of surface CH_3 groups. The surface CH_3 has two positive roles in etch reactions. First, the strength of the Al−CH_3 bond is much weaker than that of the Al−F bond. Second, the F atom in AlF_3 has a coordination number of two, whereas the CH_3 group typically favors a coordination number of one. Therefore, some chemical bonds of AlF_3 have been broken after surface modification.

Lastly, based on a detailed understanding of the reaction mechanisms, we have discussed the strategies for the design and screening of reactive precursors for thermal ALE.

[1] George, S.M. and Lee, Y. ACS Nano, 2016, 10(5), 4889-4894. [2] Natarajan, S.K. and Elliott, S.D. Chem. Mater., 2018, 30(17), 5912-5922.

4:30pm **ALE2-MoA-13 Volatile Products from Thermal Atomic Layer Etching Observed using Mass Spectrometer with Line-of-Sight Detection*, Andrew Cavanagh,*** *A Lii-Rosales, S George,* University of Colorado - Boulder

Identification of gas products from thermal atomic layer etching (ALE) is critical to understand the underlying surface chemistry. Previous quadrupole mass spectrometry (QMS) experiments identified the etch products from Al_2O_3 ALE using HF and trimethylaluminum (TMA) as the reactants [1]. These experiments sampled gas products with no line-of-sight between the substrate surface and the QMS ionizer. These QMS experiments observed dimers of the etch product, dimethylaluminum fluoride (DMAF), with itself (DMAF + DMAF) or with TMA (DMAF + TMA) [1].

For higher sensitivity and no wall-effects, a new apparatus (Figure 1) was built to provide line-of-sight between the substrate and the QMS ionizer. In this apparatus, a small reactor containing a powder sample is positioned in a larger vacuum chamber. The etch products emerge from an aperture in the reactor and are supersonically expanded into a lower vacuum region. The etch products then pass through a skimmer into the even lower pressure region containing the QMS ionizer. With this arrangement, the reactor can be maintained at ~1 Torr. The etch products can also have line-of-sight to the QMS ionizer with the ionization region at ~10^{-8} Torr.

Using this new apparatus, the ligand-exchange reaction of DMAC with AlF_3 was examined to study thermal Al_2O_3 ALE using HF and DMAC as the reactants [2]. Various monomer and dimer species were observed versus temperature (Figure 2). DMAC dimers and DMAC dimers that have undergone Cl/F exchange with AlF_3 are detected at lower temperatures. The main etch product, $AlCl_2(CH_3)$, is observed with increasing intensity at higher temperatures >230 °C. The ligand-exchange reaction of $SiCl_4$ with ZrF_4 was also examined to study thermal ZrO_2 ALE using HF and $SiCl_4$ as the reactants [3]. SiF_xCl_y species are observed from the halogen ligand-exchange reaction at >240 °C (Figure 3). $ZrCl_4$ is observed as the main Zr-containing etch product at >240 °C. $ZrFCl_3$ is detected as an additional product at higher temperatures >320 °C.

[1] J.W. Clancey, A.S. Cavanagh, J.E.T. Smith, S. Sharma and S.M. George, "Volatile Etch Species Produced During Thermal Al_2O_3 Atomic Layer Etching", *J. Phys. Chem. C* **124**, 287 (2020).

[2] Y. Lee and S.M. George, "Thermal Atomic Layer Etching of Al_2O_3, HfO_2, and ZrO_2 Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures", *J. Phys. Chem. C***123**, 18455 (2019).

[3] Y. Lee, C. Huffman and S.M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem. Mater.***28**, 7657 (2016).

5:00pm **ALE2-MoA-15 Blocking Thermal Atomic Layer Etching with Removable Etch Stop Layers*, David Zywotko,*** University of Colorado - Boulder*; O Zandi, J Faguet, P Abel,* TEL Technology Center, America, LLC*; S George,* University of Colorado - Boulder

Thermal atomic layer etching (ALE) can be performed using sequential fluorination and ligand-exchange reactions. For example, thermal Al_2O_3 ALE can be achieved using HF for fluorination and $Al(CH_3)_3$ (trimethylaluminum (TMA)) as the metal precursor for ligand-exchange [1]. Sequential exposures of HF and TMA lead to Al_2O_3 etch rates of 0.47 Å/cycle at 285°C. The ability to block thermal ALE selectively will be useful for advanced nanofabrication. This study demonstrates how thermal Al_2O_3 ALE can be blocked with removable ZrF_4 etch stop layers. In situ quartz crystal microbalance (QCM) measurements were utilized to monitor the etching and the effect of the etch stop layers.

The ZrF_4 etch stop layers could be deposited on Al_2O_3 using tetrakis(ethylmethylamido) zirconium and H_2O at 285°C. These reactants deposit ZrO_2 layers that are then converted to ZrF_4 during the subsequent HF exposure. Because $Al(CH_3)_3$ does not undergo ligand-exchange with ZrF_4 [2], the ZrF_4 layer serves as an etch stop layer. QCM measurements revealed that an initial ZrO_2 thickness of just one monolayer prior to fluorination was able to completely inhibit thermal Al_2O_3 ALE. Prior to reaching a ZrO_2 thickness of one monolayer, the etching inhibition was proportional to the ZrO_2 fractional coverage. The ZrF_4 etch stop layer was observed to arrest the thermal Al_2O_3 ALE for >100 ALE cycles.

The ZrF_4 etch stop layer could then be easily removed by a ligand-exchange reaction with $AlCl(CH_3)_2$ (dimethylaluminum chloride (DMAC)) [3]. The ZrF_4 etch stop layer could be applied and removed repeatedly without changing the Al_2O_3 etch rate. X-ray photoelectron spectroscopy (XPS) studies observed no trace of Zr on the Al_2O_3 surface after 7 cycles of DMAC and HF sequential exposures. Area selective deposition of the ZrF_4 etch stop would lead to area selective etching using HF and TMA as the reactants. Area selective deposition could be achieved based on selective reactant adsorption or substrate-dependent nucleation delays.

[1] Younghee Lee, Jaime W. DuMont and Steven M. George, "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994 (2016).

[2] Younghee Lee, Craig Huffman and Steven M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem. Mater.***28**, 7657 (2016).

[3] Younghee Lee and Steven M. George, " Thermal Atomic Layer Etching of Al_2O_3, HfO_2, and ZrO_2 Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures", *J. Phys. Chem. C***123**, 18455 (2019).

5:15pm **ALE2-MoA-16 Mechanism of the HF Pulse in the Thermal Atomic Layer Etch of HfO_2 and ZrO_2: A First Principles Study*, Rita Mullins,*** Tyndall National Institute, Ireland*; S Natarajan,* Aalto University, Finland*; S Elliott,* Schrödinger, Inc.*; M Nolan,* Tyndall National Institute, Ireland

HfO_2 and ZrO_2 are two high-k materials that are crucial in semiconductor devices. Atomic level control of material processing is required for fabrication of thin films of these materials at nanoscale device sizes. Thermal Atomic Layer Etch (ALE) of metal oxides, in which up to one monolayer of the material can be removed per cycle, can be achieved by sequential self-limiting fluorination and ligand-exchange reactions at elevated temperatures. However, to date a detailed atomistic understanding of the mechanism of thermal ALE of these technologically important oxides is lacking. In this contribution, we investigate the hydrogen fluoride pulse in the first step in the thermal ALE process of HfO_2 and ZrO_2 using first principles simulations. We also present a thermodynamic analysis approach to compare reaction models representing the self-limiting (SL) and continuous spontaneous etch (SE) processes taking place during an ALE pulse. Applying this to the first HF pulse on HfO_2 and ZrO_2 we find that thermodynamic barriers impeding continuous etch are present at ALE relevant temperatures. Explicit calculations of HF adsorption on the oxide surfaces allow us to investigate the mechanistic details of the HF pulse. A HF molecule adsorbs dissociatively on both oxides by forming metal-F and O-H bonds. HF coverages ranging from 1.0 ± 0.3 to 17.0 ± 0.3 HF/nm^2 are investigated and a mixture of molecularly and dissociatively adsorbed HF molecules is present at higher coverages. Theoretical etch rates of -0.61 ± 0.02 Å /cycle for HfO_2 and -0.57 ± 0.02 Å /cycle ZrO_2 were calculated using maximum coverages of 7.0 ± 0.3 and 6.5 ± 0.3 M-F bonds/nm^2 respectively (M = Hf, Zr).

5:30pm **ALE2-MoA-17 Thermal Atomic Layer Etching of Ta_2O_5 and TaN using BCl_3 and HF: Evidence for a Conversion-Etch Mechanism***, N Johnson,* ***Steven M. George,*** University of Colorado - Boulder

Ta_2O_5 ALE was demonstrated using BCl_3 and HF as the reactants. The Ta_2O_5 ALE surface chemistry could proceed via a fluorination and ligand-exchange mechanism or a conversion-etch mechanism. The experimental results support a conversion-etch mechanism. BCl_3 is believed to convert the surface of Ta_2O_5 to a B_2O_3 surface layer via the favorable conversion reaction $Ta_2O_5 + 10/3\ BCl_3(g) \rightarrow 5/3\ B_2O_3 + 2TaCl_5(g)$ [$\Delta G°$(250°C = -38 kcal]. HF can then spontaneously etch the B_2O_3 surface layer via the favorable reaction $B_2O_3 + 6HF(g) \rightarrow 2BF_3(g) + 3H_2O(g)$ [$\Delta G°$(250°C = -17 kcal] [1]. In contrast, HF fluorination of Ta_2O_5 to TaF_5 or $TaOF_3$ is thermochemically unfavorable.

In situ spectroscopic ellipsometry and *ex situ* x-ray reflectivity measurements were employed to study Ta_2O_5 ALE. Evidence for the conversion of Ta_2O_5 to B_2O_3 was provided by the dependence of the Ta_2O_5 etch rate on BCl_3 exposure and BCl_3 pressure. The Ta_2O_5 etch rate increased progressively with both longer BCl_3 exposures and higher BCl_3 pressures. The longer BCl_3 exposures and higher BCl_3 pressures convert more Ta_2O_5 to B_2O_3. Using three BCl_3 exposures (130 mTorr for 30 s) and one HF exposure, the Ta_2O_5 etch rate was 1.05 Å/cycle at 250°C (Figure 1). Under these conditions, the Ta_2O_5 etch rates increased with temperature ranging from 0.36 Å/cycle at 200°C to 1.96 Å/cycle at 295°C. Ta_2O_5 etch rates also increased at higher BCl_3 pressure. The etch rates varied from 0.48 to 1.46 Å/cycle using one BCl_3 exposure (30 s) at BCl_3 pressures from 130 to 1000 mTorr, respectively (Figure 2).

TaN ALE was also demonstrated using an O_3 oxidation step to oxidize TaN to Ta_2O_5. The Ta_2O_5 was then etched using BCl_3 and HF as the reactants. TaN ALE was performed using supercycles defined by an O_3 exposure followed by 60 Ta_2O_5 ALE cycles using BCl_3 and HF as the reactants. The etch rate was 38 Å/supercycle at 250°C (Figure 3). This high TaN etch rate was attributed to the large Ta_2O_5 thickness produced by O_3 oxidation. The oxidation of TaN using O_3 was studied using x-ray reflectivity measurements. TaN oxidation was observed to be fairly self-limiting at Ta_2O_5 thicknesses of 60-70 Å after longer O_3 exposures at 250°C.

[1] N.R. Johnson and S.M. George, "WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Mechanisms" *ACS Appl. Mater. Interfaces***9**, 34435 (2017).

Atomic Layer Etching
Room Arteveldeforum & Pedro de Gante - Session ALE-MoP

Atomic Layer Etching Poster Session

ALE-MoP-3 Density Functional Theory Study on the Reactions of Fluorine-Containing Molecules on Silicon Nitride Surface*, **Tanzia Chowdhury**, R Hidayat, H Kim,* Sejong University, Republic of Korea*; T Mayangsari,* Universitas Pertamina, Indonesia*; S Park,* Wonik IPS, Republic of Korea*; J Jung, W Lee,* Sejong University, Republic of Korea

Silicon nitride is one of the most extensively used silicon-based materials in semiconductor devices. It has been used as gate spacers and diffusion barriers for many decades and was recently introduced to the charge trap layer and the sacrificial layers for three-dimensional (3D) NAND devices. The integration of silicon nitride into these devices often requires selective removal of silicon nitride against other materials, such as silicon oxide or silicon, and vice versa. With the continuing device miniaturization, atomic-scale processes such as atomic layer etching (ALE) has been developed for controlled removal of thin layers. ALE consists of the modification of the surface and the removal of the modified layer. The species used to modify the surface plays a crucial role in the overall process. The ALE of silicon nitride was reported by the modification by CH_3F gas adsorption and the removal of the modified layer by Ar ion bombardment [1]. However, the comparative study on the interaction of different gaseous fluorine-based molecules with the silicon nitride surface is yet to be presented. Ab initio atomic-scale simulation can be a convenient method to study the underlying surface chemistry as well as to outline new etching process routes. Previously, we modeled and simulated the initial fluorination reactions of SiO_2 and Si surfaces by various fluorine-containing gas molecules [2]. In the present study, density functional theory (DFT) calculations have been employed to investigate the initial reaction of fluorine-containing molecules on an NH_2 and NH-terminated Si3N4 surface. We chose a comprehensive set of hydrofluorocarbons and hydrogen fluoride, such as CF_4, CHF_3, CH_2F_2, CH_3F, and HF. Surface reaction mechanisms were studied by modeling and simulation of possible reaction pathways to determine the adsorption energy, activation energy, reaction energy, and desorption energy. Finally, we compared the reactions on the Si_3N_4 surface with the reactions on the OH-terminated SiO_2 and H-terminated Si surfaces.

References

[1] W.H. Kim et al., J. Vac. Sci. Technol. A, 36, 01B104 (2018)

[2] T. Chowdhury et al., J. Vac. Sci. Technol. A, 37, 021001 (2019)

Atomic Layer Etching
Room Baekeland - Session ALE1-TuM
ALE Selectivity and Anisotropy

Moderators: Ankur Agarwal, KLA-Tencor, Sumit Agarwal, Colorado School of Mines

9:00am **ALE1-TuM-3 Highly Selective Atomic Layer Etching for Semiconductor Application***, **Akiko Hirata**,* Sony Semiconductor Solutions Corp., Japan **INVITED**

The self-limiting process is one of the most important features of atomic layer etching (ALE). The self-limiting process refers to the highly selective etching of a modified layer over a pristine substrate. One ALE cycle consists of a surface modification step and a removal step of the modified layer. In the modification step, the binding energy in the surface reactive layer is reduced so that it is easier to remove than the bulk. For the generation of a reactive layer, chemical adsorption and chemical/physical modification are generally employed. In this study, we investigate tin-doped indium oxide (ITO) and SiN ALE, and their mechanisms, to achieve the high selectivity.

ITO is a difficult-to-etch material, since the boiling points of indium halides are very high (>700 °C). Surface modification through chemical adsorption of reactive species is difficult. Thus, surface modification by energetic hydrogen ions followed by Ar desorption was proposed. The ITO was reduced by hydrogen injection, and generated an In-rich layer on the surface. The In-rich layer of ITO could be selectively etched by controlling the incident ion energy. Thus, the self-limited etching of ITO was demonstrated.

The etch rate selectivity of ITO over a mask material is indispensable for device fabrication. We intentionally controlled the amount/incubation time of Si generated from the upper electrode, and demonstrated the highly selective cyclic etching of ITO/SiO_2. The cyclic etching by area-selective surface adsorption of Si could precisely control the etch rates of ITO and SiO_2, which resulted in an almost infinite selectivity for ITO over SiO_2.

In the case of SiN ALE, the chemical adsorption of a reactive species (CH_xF_y polymer) was employed to obtain high selectivity with SiO_2 and Si. However, the SiN ALE was easily etch-stopped, owing to the excess adsorption of polymer during cyclic etching. Thus, a sequential 3-step ALE (adsorption, desorption, and O_2 ash) was proposed. After this 3-step ALE, the SiN surface was oxidized, which resulted in a fluctuation of the etched amount. To overcome these issues, plasma-enhanced conversion ALE was proposed. First, 3-step ALE was performed for SiN ALE, and the surface SiO_2 (converted from SiN by oxidation) was generated. Subsequently, highly selective SiO_2 ALE over SiN was performed. By combining highly selective SiN and SiO_2 ALE, a stable ALE process was realized.

When we use the differences in precursor incubation time among different materials effectively, highly selective etching is expected. Thus, a database of the surface adsorption of many kinds of precursors is strongly required for future highly selective ALE processes.

9:30am **ALE1-TuM-5 Aspect-Ratio Dependence of Isotropic Thermal ALE and Mitigation Thereof***, **Andreas Fischer**, A Routzahn, T Lill,* Lam Research Corp.

Advanced memory chip manufacturing is increasingly pushing the boundary toward high aspect ratio (HAR) designs in which many layers of memory cross points are stacked on top of each other. Especially in 3D-NAND memory structures, the ability to perform isotropic etches to recess high-k oxides made of hafnia or alumina or to remove excess material beneath shaded overhangs will be a critical addition to the established suite of etch and deposition processes in chip design.

In this work, we have focused on the dependence of isotropic atomic layer etching on the aspect ratio of the structures that are being etched. Utilizing the well characterized vapor-based DMAC ligand exchange mechanism, we have investigated the dependence of lateral etch rate of this process as a function of depth in nanometer-size holes of hafnium oxide. Inside these holes, we measured the horizontal etch rates and found that it slowed to a rate of 85% at the bottom of 50:1 aspect ratio holes compared to the rate at the very top of the structures for our standard ALE process.

To overcome this issue, we established that this aspect ratio dependence could be significantly suppressed by operating the process closer to saturation in the modification as well as removal step by expanding the process step time for each of the steps.

In additional experiments we found that the use of low level, zero-bias plasma can boost the etch rate in deep structures thereby reducing the aspect ratio dependence further.

We propose a simple mechanism for explaining the dependence on step time and use of plasma.

9:45am **ALE1-TuM-6 Precise Ion Energy Control with Tailored Waveform Biasing for Atomic Layer Etching***, **Tahsin Faraz**, Y Verstappen, M Verheijen,* Eindhoven University of Technology, Netherlands*; J Lopez, E Heijdra, W van Gennip,* Prodrive Technologies B.V., Netherlands*; E Kessels, A Mackus,* Eindhoven University of Technology, Netherlands

Anisotropic plasma ALE utilizes energetic and directional ions to remove any given material in a selective and self-limiting fashion.[1] However, high selectivity and etch control requires well-defined ion energies lying below the sputter etch threshold of the material, which serves as the upper limit of the so-called ion energy window of an anisotropic plasma ALE process.[2,3] In this contribution, we report on precise ion energy control – independent of the ion flux – using low-frequency (100 kHz) tailored bias voltage waveforms applied to a substrate in a commercial remote plasma reactor. Ion energies in such reactors are typically controlled by applying a radio-frequency (RF: 13.56 MHz) sinusoidal bias voltage waveform to the substrate undergoing plasma exposure. However, this yields ions with a broad energy distribution that leads to non-selective and continuous etching. Furthermore, the use of high frequency RF bias voltages entails electron heating mechanisms that do not allow for controlling the ion energy independent of the ion flux.[4] Precise ion energy control by applying a tailored bias voltage waveform[5,6] to a substrate undergoing plasma exposure is currently not employed in the field of ALE.

In this work, a prototype low-frequency bias voltage generator has been used to apply tailored bias waveforms consisting of a voltage pulse and a ramp. Such waveforms yielded ions having narrow energy distributions for energies upto 200 eV (measured using a retarding field energy analyzer, RFEA) in collisionless Ar plasmas. The energetic ions were used to sputter etch thin films of different materials (e.g. Si, SiO_2). Such investigations provide reliable experimental data on sputter etch thresholds of different materials that are typically determined by extrapolation of sputter yields measured at ion energies >> 100 eV to the low energy range,[7] which does not give accurate values. These thresholds serve as essential input (i.e. upper limits of ion energy windows) for designing novel anisotropic plasma ALE chemistries. To demonstrate the feasibility of this technique in performing anisotropic plasma ALE, a conformal SiO_2 layer on a 3D trench nanostructure was etched using directional ions whose energies were enhanced to 100 eV with tailored waveform biasing.

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Atomic Layer Etching
Room Baekeland - Session ALE2-TuM
ALE for GaN Devices

Moderators: Steven M. George, University of Colorado at Boulder, Nicolas Posséмé, CEA-Leti

10:00am **ALE2-TuM-7 GaN Damage Evaluation After Conventional Plasma Etching and Anisotropic Atomic Layer Etching***, **Simon Ruel**, P Pimenta-Barros,* CEA-Leti, France*; N Chauvet,* Lam Research, France*; F Le Roux,* CEA-Leti, France*; S Tan,* Lam Research*; F Gaucher,* Lam Research, France*; N Posseme,* CEA-Leti, France **INVITED**

GaN-based high electron-mobility transistors (HEMTs) are promising for high power device applications because of their high electric field strength, high mobility, and good thermal stability. The traditional GaN-based HEMTs is inherently normally-on because a two-dimensional electron gas (2DEG) channel is created at the AlGaN/GaN interface. As normally-off operation is desirable for commercial power applications, several structural approaches have been proposed such as recessed gate and pGaN gate. The different processing steps of GaN-based HEMTs can induce trapping effects, leading to the reduction of the 2DEG density and thus to the electrical degradation of GaN devices. In this context, plasma etching is one of the most critical step in the manufacturing of GaN devices.

In this paper, we propose to evaluate a promising Atomic Layer Etching (ALE) approach allowing to reduce or eliminate the damage compared to the conventional plasma etching.

The process investigated in this study for GaN etching consists in two steps of cyclic plasma chlorination followed by Argon or Helium bombardment. Fig 1a shows that the GaN etching is negligible after pure chlorination and pure sputtering (Ar or He plasma). GaN etching only occurs by cycling chlorination and sputtering steps, meaning that the basic concept of ALE is demonstrated for both ALE Ar and He. The etch per cycle (EPC) of ALE Ar and He is 0.5nm/cy and 1.1nm/cy respectively. Therefore, ALE He is faster than ALE Ar whereas a same bias voltage of 50V has been applied. After plasma parameters optimization, Fig 1b shows that the ideal ALE Ar and ALE He process window in term of ion energy is between [70-100V] and [50-80V] respectively. XPS analyses and roughness studies by AFM (Fig 2a and b, respectively) reveal a very similar surface state after etching with ALE or Steady only.

The plasma induced damage has also been evaluating for both ALE processes on blanket wafers and compared to the steady process. Fig 3 shows that, for a similar over etch, ALE He induces higher R_{sheet} degradation than ALE Ar. This result can be explained by deeper He ion penetration within the substrate compared to Ar ion as the He ions are lighter. While ALE Ar presents a lower R_{sheet} than the steady process, confirming a lower film damage induced by ALE process compared to the steady process.

10:30am **ALE2-TuM-9 Analysis of Ion Energy Dependence of Depth Profile of GaN by In-situ Surface Analysis***, M Hasagawa,* ***Takayoshi Tsutsumi,*** Nagoya University, Japan*; A Tanide, S Nakamura,* SCREEN Holdings Co., Ltd., Japan*; H Kondo, K Ishikawa, M Hori,* Nagoya University, Japan

In fabrication of the next-generation power electronic devices of gallium nitride (GaN), an atomic layer etching (ALE) technique with cyclic processes of ion irradiation and Cl adsorption steps has been attracted for reduction of plasma induced damage. To control surface stoichiometry of GaN in the ALE, we focus on the ion energy dependence of the depth profile of GaN at each Ar and Cl reaction step using the beam experiments with *in situ* X-ray photoelectron spectroscopy (XPS).[1,2]

The plasma beam system was used for Cl adsorption and Ar ion irradiation process. The as-cleaned surface was exposed by Cl radicals with a dosage of 10^{19} cm^{-2} generated in Cl_2 gas (flow rate 0.5 sccm) plasma by application of RF power of 400 W, while the shutter was placed in front of the sample to block the Cl ion to the surface. The Ar ion energy, that has a narrow ion energy distribution, was specified by applying a direct current (dc) voltage bias to the acceleration electrode. The one cycle consisted of these Ar ion irradiation and Cl radical exposure. To stabilize the GaN surface, five cyclic processes were carried out. Then, the GaN surface at each step was analyzed by angle-resolved *in-situ* XPS. Depth profiles of atomic concentration were estimated by the maximum entropy method.

Figure 1 show the depth profile of Ga-Ga and Ga-Cl bond distribution GaN after 5th Ar irradiation and 6th Cl adsorption process at accelerated voltages of 100 and 200 V. After Ar ion irradiation, Ar ion irradiated depth where concentration of Ga-Ga decreased by 1/e of maximum concentration is increased by Ar ion energy. After Cl radical exposure, Cl penetration depth where concentration of Ga-Cl and Ga-Cl_2 decreased by 1/e of maximum concentration is similar to Ar ion irradiated depth. This suggests that chlorinated layer thickness relates to damaged layer thickness. As a result, the etched depth would be predominantly determined by the damaged layer thickness. Namely, the etch depth is enabled to control by the ion energy in the Ar ion irradiation cycle.

[1] T. Takeuchi et al., J. Phys. D: Appl. Phys. 46, 102001 (2013).

[2] Y. Zhang et al., J. Vac. Sci. Technol. A 35, 060606 (2017).

10:45am **ALE2-TuM-10 Atomic Layer GaN Etching by HBr Neutral Beam***, S Samukawa,* ***Takahiro Sawada****, D Ohori,* Tohoku University, Japan*; K Sugawara, M Okada, K Nakata, K Inoue,* Sumitomo Electric Industries, Ltd., Japan*; D Sato, H Kurihara,* Showa Denko K.K., Japan

Refining AI/IoT techniques is absolutely essential for developing smart and sustainable societies. The amount of information in networks is becoming larger and larger as time goes on, and wireless high-speed and large-capacity data communication technologies such as 5G and beyond are key for processing big data. AlGaN/GaN high electron mobility transistors (HEMTs) are promising for both high-power and high-frequency applications because their two-dimensional electron gas (2DEG) has high saturation velocity, high mobility, and high carrier concentration with a high breakdown field. Although AlGaN/GaN HEMTs have many advantages, normally-off operation for GaN HEMTs is still a big challenge. In the gate-recess, normally-off operation is achieved by removing the barrier layer by dry etching to reduce the 2DEG concentration under the gate electrode. Thus, an atomic layer and defect-free etchings for GaN are indispensable to achieve high-frequency, high-power, and normally-off operation. In this work, we investigated atomic layer defect-free GaN etching by using Cl_2 and HBr neutral beams.

GaN etching rates and etching products on the substrate surface were investigated by using Cl_2 or HBr neutral beams with the beam acceleration bias power from 0 to 20 W. The gas flow rate and substrate temperature were fixed to 40 sccm and –20 ºC, respectively. To analyze the surface atomic layer etching reactions, we measured the Ga3d signal by X-ray photoelectron spectroscopy (XPS) and found that the surface composition ratio consisted of four kinds of peaks (Ga-Cl_3 or Ga-Br_3, Ga-O, Ga-N, and Ga metal) using Gaussian peak fitting. With the Cl_2 neutral beam, the Ga-O ratio (Ga dangling bond) increased, and the Ga-N ratio (GaN) decreased with bias power increases. The Ga-Cl3 ratio (etching product) did not significantly change, regardless of the bias power. In contrast, with the HBr neutral beam, higher Ga-N and lower Ga-O ratios could be achieved in spite of the high bias power, and the Ga-Br_3 ratio (etching product) was increased with increasing the bias power. The HBr neutral beam could make a thinner surface product layer than the Cl_2 neutral beam because the atomic size of Br is larger than that of Cl. The Cl_2 neutral beam had a five times higher etching rate than that of the HBr neutral beam at 20 W of beam acceleration bias power. These results suggest that $GaBr_3$ is a more involatile product and that the GaN surface is protected by the $GaBr_3$ layer. We found that HBr neutral beam etching could obtain more precise atomic layer level neutral beam assisted etching with the thinner and more involatile etching product layer.

Atomic Layer Etching
Room Baekeland - Session ALE1-TuA

ALE of Si-based Materials

Moderators: Thorsten Lill, Lam Research Corporation, Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation

1:00pm **ALE1-TuA-1 Realizing Selective Material Removal in Plasma-Based Atomic Layer Etching (ALE)*, Gottlieb Oehrlein,*** University of Maryland **INVITED**

In atomic layer etching (ALE) one applies iteratively sequences of cycles consisting of reactant supply and surface reaction steps to establish self-limited material removal approaching atomic scale. Since for ALE the reactant is injected only during the surface functionalization step, the surface changes continuously which has important implications for achieving materials etching selectivity. We will discuss several examples of how high materials etching selectivity in ALE may be achieved. In a first approach we describe the use of complex fluorocarbon film precursors to achieve highly selective ALE of SiO_2 over various underlayers. Additionally, reactants during the deposition step may exhibit substrate-selective deposition based on the chemical affinity of precursor gases to the substrate and nature of interfacial bonding. Combining substrate-selective deposition with a surface reaction step provides a new approach for achieving material-selective ALE, and we will describe results selective removal of HfO_2 over Si surfaces. Another material system that can be improved via ALE processing is that of maximizing the etching selectivity of a hard mask material like SiO_2 to extreme ultraviolet (EUV) photoresists in a pattern transfer process, and will be briefly reviewed.

Acknowledgements

I gratefully acknowledge the contributions and collaboration of K.-Y. Lin, A. Pranda, C. Li, D. Metzler, S. Engelmann, R. Bruce, and E. Joseph to this work, and would like to thank Semiconductor Research Corporation (Task No. 2017-NM-2726) and National Science Foundation (CBET-1134273) for funding.

1:30pm **ALE1-TuA-3 Atomic Layer Etching of SiO_2 and Si_3N_4 with Fluorocarbon, Hydrofluorocarbon, Fluoroether and Fluoroalcohol Compounds*, Yongjae Kim,*** *S Kim, H Kang, Y Lee, H Chae,* Sungkyunkwan University, Republic of Korea

Highly precise etching technologies are required to etch nanometer scale patterns and to achieve high selectivity in atomic level etching. [1-3] In this work, cyclic plasma atomic layer etching process was performed for SiO_2 and Si_3N_4 with surface modification in an inductively coupled plasma (ICP) reactor with fluorocarbon, hydrofluorocarbon, fluoroether and fluoroalcohol plasmas. Etch rate were compared at various conditions of plasma power and reaction gases. The process consists of two steps of surface modification and removal step. In the first step, fluorocarbon(FC) layers were deposited on SiO_2 and Si_3N_4 surface with fluorocarbon, hydrofluorocarbon, fluoroether, and fluoroalcohol plasmas. In the second step, the modified layers are removed with ions or radicals generated from Ar or O_2 plasmas. The etch rate was correlated with the fluorine-carbon (F1s/C1s) ratio determined from XPS peaks. Fluoroether and fluoroalcohol plasma generated FC layers having the lowest F1s/C1s ratio, and C_4F_8 plasmas produced the highest F1s/C1s ratio. Constant etch rates were observed in the bias voltage range of 55–60 V, which is identified as the ALE window. Self-limiting etch rate was confirmed with the etching process time and the etch rate could be controlled below 10 Å/cycle. High selectivities of SiO_2/Si and Si_3N_4/Si were obtained with fluoroether precursor having low F1/C1s ratio and the higher carbon on surface is attributed to the lower Si etch rate.

References

[1] V. M. Donnelly and A. Kornblit, J. Vac. Sci. Technol., A 31, 050825 (2013).

[2] H. Zhu, X. Qin, L. Cheng, A. Azcatl, J. Kim and R. M. Wallace, ACS Appl. Mater. Interfaces 8, 19119 (2016).

[3] Y. Lee and S. M. George, ACS Nano 9, 2061 (2015).

Keywords: Cyclic plasma etching, Fluorocarbon polymer, Selectivity

1:45pm **ALE1-TuA-4 Strategies to Enhance the Etch Selectivity During Plasma–Assisted Atomic–Scale Etching of SiO_2 over SiN_x*, Ryan Gasvoda,*** Colorado School of Mines*; Z Zhang, E Hudson,* Lam Research Corp.*; S Agarwal,* Colorado School of Mines

Atomic layer etching (ALE) and its derivatives can provide high etch fidelity, atomic–scale precision, directionality, and high selectivity that is required for manufacturing of sub–7–nm node semiconductor devices. Specifically, plasma–assisted ALE of SiO_2 and SiN_x with ultra–high selectivity of SiO_2 to SiN_x is required in the self–aligned contact etch step. Generally, high selectivity can be achieved through manipulating the process and plasma parameters (similar to continuous etching). To further increase overall etch selectivity, we selectively functionalize the SiN_x surface with benzaldehyde prior to the start of etching. This pre–functionalization retards the net etch of SiN_x in the subsequent ALE process leading to higher SiO_2 to SiN_x etch selectivity. This etch selectivity can be reversed by selectively functionalizing the SiO_2 surface.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy in combination with *in situ* 4–wavelength ellipsometry to monitor surface reactions, film composition as well as etch per cycle during ALE. Further, the ion energy distribution (IED) in the Ar plasma activation half–cycle is characterized with a retarding field energy analyzer. We have shown previously that cyclic azasilanes can be used to selectively functionalize the SiO_2 surface from the gas phase. Figure 1 shows the infrared active region of a SiN_x (green) and SiO_2 (blue) surface exposed to benzaldehyde which selectively functionalizes the SiN_x surface with sp^2–hybridized–carbon. Figure 2 shows the infrared absorbance change for 15 sequential ALE cycles on a) bare SiN_x surface and b) benzaldehyde functionalized SiN_x. In both cases, we observe a broad increase in absorbance from ~1200 – 1800 cm^{-1} which indicates the formation and accumulation of an etch inhibiting graphitic fluorocarbon film. An etch stop is observed at cycle 13 for both SiN_x surfaces, however the net etch of SiN_x is ~20% less (~2 nm) for the benzaldehyde functionalized SiN_x than the net etch of the bare SiN_x. This shows that pre–functionalizing a SiN_x surface, selective to a SiO_2 surface, can reduce the overall SiN_x etch loss. Further, we discuss the role of maximum ion energy and IEDs in the activation step on overall etch selectivity with specific focus on non–ideal Ar plasma activation steps where the maximum ion energy is above the sputtering threshold of both SiO_2 and SiN_x.

2:00pm **ALE1-TuA-5 Cryo-ALE of SiO_2 with C_4F_8 Physisorption: Process Understanding and Enhancement*, Gaëlle Antoun,*** *T Tillocher, P Lefaucheux, R Dussart,* GREMI Université d'Orléans/CNRS, France*; A Girard, C Cardinaud,* IMN Université de Nantes/CNRS, France*; K Yamazaki,* Tokyo Electron Limited, Japan*; J Faguet, K Maekawa,* TEL Technology Center, America, LLC

Cryogenic Atomic Layer Etching (Cryo-ALE) is a different approach for ALE, proposed in order to limit drifts due to reactor wall contamination during a process. The proof of principle has been performed on SiO_2 using a fluorocarbon gas and presented in [1].In this process, C_4F_8 is injected in gas phase, and physisorbs on the cooled surface of the substrate. Then Ar plasma is initiated in order to activate the etch. However, in [1], the authors demonstrated the possibility to achieve the etching only at -120°C in their experimental conditions. The aim of this paper is to better understand the mechanisms involved in Cryo-ALE in order to enhance the process and increase the operating temperature.

In order to achieve this work, an ICP reactor has been used. An in-situ ellipsometer as well as an Electrostatic Quadrupole Mass Spectrometer (QMS) are coupled to the reactor. The ellipsometer is used in kinetic mode in order to follow the thickness variation during the process. The QMS is used to follow some species in Multiple Ion Detection (MID) mode. Tests were all performed on SiO_2 coupons glued on SiO_2 6" carrier wafers.

In addition, for surface characterization, quasi in-situ X-Ray Photoelectron Spectroscopy (XPS) measurements were also performed. The ICP reactor used here is different and the substrate is moved from the reactor to the XPS chamber with a transfer rod while keeping the substrate at low temperature.

In order to understand the mechanisms involved in Cryo-ALE, QMS tests were first performed by injecting a C_4F_8 gas flow during one minute on a cooled surface. The substrate temperature and the pressure of C_4F_8 were then varied in order to determine their influence on the surface residence time of C_4F_8. Those tests were also followed by ellipsometry in order to monitor the thickness physisorbed on the substrate surface. XPS tests in same conditions were performed and correlated with QMS results. Indeed, it has been demonstrated that decreasing temperature increases the C_4F_8

surface residence time and hence increases the concentration of fluorine at the surface.

With those data, it was possible to perform new cryo-ALE cycles by increasing the temperature to -90°C. Hence, very regular 150 cryo-ALE cycles were achieved with an etching amount of 0.13 nm/cycle.

The authors would like to thank S.Tahara for all the discussions that helped contributing to those results.

[1] G. Antoun, P. Lefaucheux, T. Tillocher, R. Dussart, K. Yamazaki, K. Yatsuda, J. Faguet, and K. Maekawa, Appl. Phys. Lett. **115**, 153109 (2019).

2:30pm **ALE1-TuA-7 Interpretation of SiO_2 Atomic Layer Etching via a Simple Analytic Model***, **Youngseok Lee**, I Seong, J Lee, S Lee, C Cho,* Chungnam National University, Korea*; S Kim,* Nanotech, Korea*; S You,* Chungnam National University, Korea

We established a simple analytic model of SiO2 thickness changes during SiO_2 atomic layer etching (ALE) and analyzed our experimental data of sample thickness change trends at various ALE conditions via our model. SiO2 ALE experiments were conducted with C4F8/Ar inductively coupled plasma by admitting C4F8 gas into continuous Ar plasma for surface modification (reaction A) of the SiO_2 surface and turning the C4F8 gas off for removal of the modified surface (reaction B) by the Ar plasma ion bombardment. During that process, the thickness change of the SiO_2 samples was monitored using an in-situ multi-wavelength ellipsometer, which showed an increase of the total sample thickness including that of a fluorocarbon (CFx) film deposited on the SiO_2 surface during reaction A and a decrease during reaction B. Then, the ellipsometric results were fitted with our analytic model, which is based on the mechanism of conventional SiO_2 etching using CFx plasma that has previously been understood in detail. As a result, our model could explain several characteristic trends of the sample thickness change under different conditions, and the trends seemed to be mainly related to the deposition rate of CFx film on the SiO_2 surface. The higher CFx film deposition rate is expected to lead to more desirable ALE results. In addition to experimental data analysis, useful insights for advanced SiO_2 ALE could be achieved through the model, helping to decide the optimized ALE condition. In this presentation, physical validity of the model and SiO_2 ALE interpretation that was obtained by the model will be discussed.

Atomic Layer Etching
Room Baekeland - Session ALE2-TuA

Novel ALE Techniques and Materials

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Alok Ranjan, TEL Technology Center, America, LLC

4:30pm **ALE2-TuA-15 Novel Chemistries for Layer-by-Layer Etching of 2D Semiconductor Coatings and Organic-Inorganic Hybrid Materials***, **Anil U. Mane**, M Young, D Choudhury, S Letourneau, A Yanguas-Gil, J Elam,* Argonne National Laboratory **INVITED**

Here we report two new advances in atomic layer etching (ALEt) that extend our range of capabilities in nanoscale device fabrication. Semiconductor device manufacturing is limited by our ability to precisely deposit and remove thin film layers at the various levels of multistep device fabrication processes. Consequently, innovations in atomic layer deposition (ALD) and etching methods are essential. ALD-based methods have matured significantly and are now used extensively in semiconductor fabs. Recently, there has been an intense focus on developing ALEt methods. In particular, thermal ALEt has been shown to precisely remove ALD inorganic thin films selectively and on complex structures. These capabilities have opened new possibilities for nanoscale device design. Here, we report a new thermal etching process similar to ALEt for removing hybrid inorganic-organic layers that we call molecular layer etching (MLEt) [1]. This MLEt process uses vapor phase lithium organic salts in combination with trimethyl aluminum to perform layer-by-layer etching of molecular layer deposition (MLD) coatings. Ultra-thin layers of two dimensional (2D) transition metal dichalcogenide (TMD) semiconductors can exhibit exceptional electrical, optical, magnetic, mechanical and chemical properties. This allows the exploration of internal quantum degrees of freedom of electrons and their potential application in optoelectronic, energy, and sensor devices. Among the various 2D-TMDs, MoS_2 has shown exciting material properties and this has stimulated the exploration of a variety thin film synthesis methods such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and solution based methods. In addition, the ALD community is investigating ALD methods for MoS_2 growth [2-3]. Here we report the thermal ALEt of ALD MoS_2 thin films [4]. We believe the successful combination of both ALD and ALEt of MoS_2 and other TMDs can pave the way to control the synthesis of 2D-TMD layers over large areas. Combining ALD and ALEt will allow MoS_2 interface engineering and enable MoS_2 integration into the large-scale manufacturing of future complex device structures.

[1] Molecular Layer Etching of Metalcone Films Using Lithium Organic Salts and Trimethylaluminum,

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[2] Atomic layer deposition of molybdenum disulfide films using MoF_6 and H_2S,

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