Atomic Layer Etching
Room Hall 3 - Session ALE-SuP
Atomic Layer Etching Poster Session

ALE-SuP-1 Removing Defects from InGaP Surfaces Using Thermal Atomic Layer Etching (ALE)*, R. Edel, **Andrew Cavanagh**, T. Nam, S. George,* University of Colorado Boulder

Indium gallium phosphide (InGaP) is widely used for red light-emitting diode (LED) devices. Surface defects on LED devices can lead to non-radiative electron/hole pair recombination that reduces their light output. This light quenching effect is more severe for smaller LED devices that have high surface-to-volume ratios. The surface defects are believed to be formed by energetic ion species from plasma processing used to fabricate the LEDs. Thermal ALE may provide a method to remove these surface defects.

Thermal InGaP ALE was performed using static, sequential hydrogen fluoride (HF) and dimethylaluminum chloride (DMAC) exposures. This procedure yields etch rates of 0.5–1.0 Å/cycle at temperatures from 300–330 °C, respectively. Etching with only HF/DMAC exposures often produced a chemically distinct top layer due to a conversion mechanism. This conversion could be avoided by first removing the InGaP native oxide using sequential HF and trimethylaluminum (TMA) exposures. This work was conducted using a new apparatus that combines a hot wall ALD/ALE reactor with *in vacuo* Auger spectroscopy. This apparatus allows the sample to be characterized throughout the thermal ALE process without exposure to air.

The removal of surface defects by ALE was studied using *ex situ* X-ray photoelectron spectroscopy (XPS). InGaP samples damaged by Ar^+ ion sputtering were analyzed before and after thermal ALE by tracking the shifted components in the P 2p XPS region that correspond to damage from sputtering. An XPS scan of an unsputtered InGaP sample shows only a bulk doublet (Figure 1a). An InGaP sample after sputtering displays two additional shifted components that correspond to undercoordinated atoms in the damaged lattice (Figure 1b).

InGaP ALE can then remove the XPS features associated with the damaged lattice. A bulk-like XPS spectrum showing minimal damage was recovered after 50 ALE cycles for a sample initially exposed to 500 eV sputtering (Figure 2a). By contrast, annealing for 72 hours at 300 C without etching was not sufficient to eliminate the damage. AES analysis similarly showed that the argon implanted in the sample by sputtering was removed after etching but not annealing. Increasing the sputtering ion energy to 2 keV required more extensive etching to remove the sputter damage. With the higher ion energy of 2 keV, 100 ALE cycles were able to largely remove the surface defects (Figure 2b). The etch depth consistent with 100 ALE cycles indicates a damaged material depth of ~4-5 nm.

ALE-SuP-2 Tailored Waveforms for CCP Discharges in ALE Applications*, **Anna Nelson**, S. Mohr,* Quantemol Ltd., UK

Atomic layer etching (ALE) is increasingly used in the manufacturing of semiconductor tools as they give more control over the resulting etching profiles than traditional etching techniques. While different approaches to ALE exist, many of them employ plasmas in one or more steps of the ALE process, be it to use the neutral radicals produced in the plasma to alter the surface or the ions to remove the altered top layer [1].

For such applications, independent control of ion flux and ion energy is highly desirable. Single frequency capacitively coupled discharges (CCPs) do not offer this, as the input power affects both flux and energy. Dual frequency discharges allow this to some extent, but it is limited due to, for example, increased ionization by secondary electrons at high powers of the low frequency. Furthermore, traditional CCPs usually produce bimodal ion energy distribution functions which can cover several 10s to 100s of eV with sharp peaks at either end, so the ion energy cannot be easily limited to a small interval of energies, which is desirable especially for ALE applications, so that the ions remove the top layer of the surface but do not damage the underlying bulk [1].

An alternative approach to achieve this desired control are tailored waveforms. These can range from so-called asymmetric waveforms combining a fundamental frequency with even multiples [2] to non-sinusoidal waveforms typically consisting of sharp voltage peaks [1] followed by a relatively long interval of an almost constant voltage. While it has been demonstrated that these type of CCPs offer independent control of ion flux and energy and/or are able to limit the ion energy to narrow energy intervals, they have not yet been well studied in industrial applications.

This presentation will show first efforts to simulate industrial applications of tailored waveform CCPs using the well-established 2D plasma simulation code HPEM [3]. The simulations are carried out in gases used in typical ALE applications such as chlorine containing molecules whereas most investigations so far were limited to rare gases such as argon which give principle insight into the effects taking place in such discharges are of limited use to understand and optimize industrial processes. We will demonstrate first results from these simulations.

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ALE-SuP-3 Atomic Layer Control of 2D WS_2 Through the Formation of Volatile Tungsten Oxychloride*, **Hye Won Han**, J. Kang, J. Kim, G. Yeom,* Sungkyunkwan University, Republic of Korea

Transition metal dichalcogenides (TMDs) are two-dimensional materials renowned for their variable electronic and optoelectronic properties depending on the thickness of the materials. Precise layer control of two-dimensional TMDs is crucial for their integration into advanced material and device applications, necessitating a refined etching technique. Previous research approaches to layer control using radical adsorption and ion desorption processes, which can cause physical damage. To address these challenges, we introduce the layer control of WS_2 with the formation of volatile tungsten oxychloride designed for the sequential removal of WS_2 layers. Oxychloride is formed on the WS_2 surface using an ALE-based cyclic sequential process and the volatile tungsten oxychloride can be removed by heating. Utilizing a radical-only mechanism, we can ensure damage-free and isotropic etching, which is essential for three-dimensional device fabrication. By offering the layer control of WS_2, this research opens new avenues for the integration of TMDs into future material and device technologies, marking a significant advancement in the field of advanced materials research.

ALE-SuP-4 Thermal Atomic Layer Etching of Ternary Indium Gallium Phosphide Based on Fluorination and Ligand-Exchange Reactions*, **TAEWOOK NAM**, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) has been developed for metal oxides (Al_2O_3, HfO_2, ZrO_2, ZnO, WO_3, SiO_2), nitrides (SiN, TiN, AlN), elements (Ni, Co, Mo, Si, W), and sulfides (ZnS). This study introduces the thermal ALE of a ternary phosphide material – indium gallium phosphide (InGaP). The InGaP films were grown on GaAs (100) substrate using metal organic chemical vapor deposition (MOCVD). The thickness of the InGaP films was monitored during thermal ALE by spectroscopic ellipsometry (SE). InGaP ALE was first demonstrated using hydrofluoric acid (HF) and dimethylaluminum chloride (DMAC). HF and DMAC exposures under viscous flow conditions did not etch InGaP. However, with static 100 mTorr and 1 Torr exposures of HF and DMAC, respectively, InGaP was etched at 0.6 Å/cycle after a short etch delay. The etching delay is presumably caused by native oxide on the InGaP surface. At 200 °C, the etch rates were 0.05, 0.15, 0.41, 0.6, and 1.12 Å/cycle, at 225, 250, 275, 300, and 325 °C, respectively. After ALE, Auger electron spectroscopy (AES) detected Al on the InGaP surface. The Al AES signal indicates there could be a conversion reaction between the DMAC precursor and InGaP. Another etching chemistry was also developed for InGaP ALE using xenon difluoride (XeF_2) and boron trichloride (BCl_3). These precursors increased the etch rate and decreased the etching temperature compared with HF and DMAC. At XeF_2 and BCl_3 pressures of 20 and 230 mTorr, InGaP ALE showed linear thickness decrease versus ALE cycles after a short etch delay. When the XeF_2 and BCl_3 dose times were 1.5 and 1 s, respectively, the etch rate of InGaP at 200 °C was 2.2 Å/cycle. The etch rate saturation versus precursor dose times was also characterized at 175 °C. The etch rate was saturated at 2.5 Å/cycle when the XeF_2 and BCl_3 dose times were ≥ 1.5 and ≥1 s, respectively. The larger etch rates and lower etching temperatures using XeF_2 are attributed to more favorable fluorination with XeF_2. From thermochemical calculations, fluorination of InP and GaP using HF at 200 °C has standard Gibbs Free Energies of DG° = -39 and -26 kcal/mol. In contrast, fluorination using XeF_2 has much larger standard Gibbs Free Energies of DG° = -424 and -411 kcal/mol, respectively.

ALE-SuP-5 Spontaneous Etching of Group V and VI Metal Oxides by Deoxychlorination Using Thionyl Chloride*, **Troy Colleran**, S. George,* University of Colorado at Boulder

Group V and VI metals and their respective oxides are of interest in microelectronic, electrochemical and sensing devices. Thermal etching of these materials provides a method to fabricate and clean these devices. The spontaneous etching of Group V and VI metal oxides was studied using

an apparatus equipped with a quadrupole mass spectrometer (QMS). The QMS could measure the volatile etch products produced during thionyl chloride ($SOCl_2$) exposure to nanopowders of Group V and VI metal oxides. Spontaneous thermal etching of MoO_3, WO_3, WO_2, VO_2, V_2O_5, and Nb_2O_5 was observed during $SOCl_2$ exposures at 200°C. Etching was monitored by the presence of volatile metal oxychlorides during $SOCl_2$ exposures in combination with the measured mass losses of the nanopowder after $SOCl_2$ exposures. No etching was detected on MoO_2 or Cr_2O_3.The volatile etch products were different dependent on the oxidation state of the metal center in the metal oxide. Species in the form of MO_2Cl_2 were most common for metals in the +6 oxidation state, such as MoO_3 or WO_3. Exclusively $MOCl_3$ species were observed from metals in the +5 oxidation state. Lower oxidation states acted as a barrier as illustrated by the inability of MoO_2 and Cr_2O_3 to undergo spontaneous etching. However, in the case of WO_2 and VO_2, $SOCl_2$ was able to perform as an oxidizing agent and produced WO_2Cl_2 and $VOCl_3$ etching products, respectively. The ability to spontaneously etch these metal oxides provides a method for cleaning the native oxides from pure Group V and VI metal films. In addition, combined with an oxidation step, the spontaneous etching of these metal oxides provides a pathway for metal ALE.

ALE-SuP-6 Phase Transition of Molybdenum Disulfide by Controlled Ion Beam ALE Method*, **Ji Eun Kang**, H. Han, J. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Among the two-dimensional transition-metal dichalcogenides (TMDs), molybdenum disulfide (MoS_2) exhibits promising capabilities for advanced electronic and optoelectronic devices. However, the performance of these devices is often hindered by the Schottky barrier and contact resistance issues arising from the interface between TMD materials and metal electrodes. To address this challenge, various techniques such as alignment of metal work functions, lithium intercalation, application of strain, and colloidal synthesis have been explored. Despite their potential, achieving uniform application of these techniques across large areas remains as a challenge. A novel strategy employing defect engineering to facilitate a phase transition from the 2H to the 1T phase has emerged to reduce contact resistance. But time-dependent processes and uncontrolled energy sources in these methods makes it difficult to uniformly create chalcogen defects in TMDs, potentially compromising the quality of the 1T phase. In this study, a self-limiting technique used for MoS_2 ALE that precisely employs controlled Ar ion beams was investigated to selectively remove the top sulfur layer of MoS_2, ensuring a uniform metal transition (MT) of MoS_2 with a defined threshold ion energy. Furthermore, the conversion from the 1T phase back to the p-type branch was investigated through the incorporation of nitrogen atoms at the sites of removed sulfur, offering a novel approach to enhance the electronic properties of MoS_2.

ALE-SuP-8 Ab Initio Investigation of Chelation on Amorphous $CoCl_2$ Films for Atomic Layer Etching*, **Eugene Huh**, S. Lee,* Ewha Womans University, Republic of Korea

A thermal atomic layer etching process for Cobalt (Co) has been developed using Chlorination with BCl_3 and Chelation with Hexafluoroacetylacetone (Hhfac). A thermal atomic layer etching process for Cobalt (Co) has been developed using Chlorination with BCl_3 and Chelation with Hexafluoroacetylacetone (Hhfac). A previous computational study focused on DFT research about the chelation of adsorption and desorption of Hhfac, using the $CoCl_2$ flakes model, as the coordination with Cl atoms proceeds through the termination of Co atoms on the amorphous surfaces. It was confirmed that the chlorination process is most stable when four Cl atoms form a coordination bond with Co, and the chelation process is most stable when CoCl2hfac and HCl are formed and then removed. Additionally, it was revealed that the adsorption of Hhfac during the chelation process is the rate-determining step.

In this study, we investigate the processes of chlorination and chelation with Hhfac on amorphous Co surfaces by performing DFT calculations. To this end, we perform the Monte Carlo simulations and Ab initio Molecular Dynamics (AIMD) to generate the various amorphous Co structures. Subsequently, we performed DFT calculations to obtain thermodynamic information about the chlorination of amorphous Co according to the Cl atom ratio and chelation process through coordination with Hhfac. On the amorphous $CoCl_2$ surface, it was observed that structures with low coordination numbers, similar to the $CoCl_2$ disk model, are energetically stable. Unlike in the disk model, it was identified that Co-Co bonding influences these structures. Such computational results enhance our understanding of atomic layer etching in experimentally obtained amorphous Co structures.

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ALE-SuP-9 Selective Isotropic Atomic Layer Etching of Silicon Nitride over Silicon Oxide with Surface Fluorination using CF_4/H_2O Plasma and Heating*, **Daeun Hong**, H. Lee, M. Jeon, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

In this work, highly selective isotropic atomic layer etching (ALE) process was developed for Si_3N_4 over SiO_2 by forming ammonium fluorosilicate (AFS) using CF_4/H_2O plasma and by removing the modified layer with heating. The AFS layer was selectively formed on Si_3N_4 surface with CF_4/H_2O plasma in the modification step, and the AFS layer was decomposed by heating in the removal step. The effect of the CF_4/H_2O gas ratio on the AFS formation was investigated in the modification step. The AFS layer was formed on Si_3N_4 over a wide range of H_2O/ (CF_4+H_2O) ratios from 46 % to 82%, but the layer was partially removed into NH_3, SiF_4, and HCN with excessive H radicals at the H_2O/ (CF_4+H_2O) ratios of 75% and above. The removal characteristic of AFS was investigated depending on the heating temperature in the removal step. The AFS was totally decomposed at a temperature of 200 ℃ or higher. The infinite etch rate selectivity of Si_3N_4 over SiO_2 was achieved at the H_2O/ (CF_4+H_2O) ratios above 70%. The high selectivity was attributed to the decrease in F radicals as the H_2O flow rate increases by preventing spontaneous etching of SiO_2 at the high H_2O ratio. Etch per cycle of Si_3N_4 was saturated to 7 nm/cycle after 20 min of AFS formation time with H_2O/ (CF_4+H_2O) ratio of 70%. No carbon residues were observed on the Si_3N_4 surface after the ALE process with CF_4/H_2O plasma.

ALE-SuP-10 Selective Thermal Atomic Layer Etching of Molybdenum & Other Metals for Semiconductor Metallization*, M. McBriarty, N. Vu, **Bhushan Zope**,* Merck KGaA, Darmstadt, Germany

Performance of semiconductor integrated devices continues to be limited by metallization scaling. Molybdenum will play a key role in device scaling and is being evaluated for applications in logic interconnect, 3D-NAND word-line, and DRAM word-line. Mo enables low resistivity films while also eliminating the need for high-resistivity barriers, further accentuating its resistivity benefit to the metallization stack.

Selective thermal atomic layer etching (ALE) of molybdenum is critical for the successful integration of molybdenum metal in integrated device manufacturing. We have identified thermal ALE methods to selectively etch Mo metal without etching dielectric (SiO2) or semiconductor (Si) films. Mo etch is achieved by either oxidizing or chlorinating the Mo surface, followed by thermochemical volatilization of Mo complexes. Surface-limited reactions provide Mo etching without compromising its resistivity and enable consistent etch in high aspect ratio features. Surface quality is preserved, indicated by minimal surface roughening or contamination.

By demonstrating multiple pathways for Mo thermal ALE, we enable manufacturers to choose an ALE process that is suitable for a given device integration. We also extend these thermal ALE methods to other metals of interest, including Co, W, and TiN.

ALE-SuP-11 Theoretical investigation on Plasma Decomposition and Recombination Reaction Characteristics of C_4F_8O Isomers as Alternatives to HFC*, **Mihyeon Jo**, S. Lee,* Ewha Womans University, Republic of Korea

As we progress towards a carbon-neutral society, there is a growing emphasis on utilizing semiconductor etching gases with reduced global warming potentials. This necessitates the exploration of alternative gases to replace conventional perfluorinated compounds (PFCs) currently employed in industrial processes. Oxygen-containing fluorocarbons have emerged as promising candidates for this role due to their lower propensity to generate environmental pollutants such as CO, CO2, and COF2. In this context, the potential utilization of compounds like Perfluoro-2-butanone and Perfluorotetrahydrofuran in ion plasma etching processes is of particular interest. These compounds offer the possibility of maintaining high process efficiency while minimizing environmental impact.

In this study, we theoretically investigate and compare the decomposition and recombination characteristics of the three isomers of C_4F_8O: Fluoro-ketone derivatives, Perfluoro-2-butanone, and Fluoro-epoxide derivatives, perfluoroisobutylene oxide, as well as the ring compound

Perfluorotetrahydrofuran, using the Gaussian 16 software program. Additionally, our study aims to provide comprehensive insights into the decomposition and recombination pathways of neutral molecules, as well as ionization-induced decomposition pathways. By examining these aspects, we seek to offer a thorough understanding of the chemical transformations occurring during the decomposition and recombination processes of the investigated Fluoro-ketone and Fluoro-epoxide derivatives, as well as Perfluorotetrahydrofuran. This holistic approach allows for a detailed analysis of both neutral-state and ionization-induced reactions, shedding light on the intricate mechanisms governing the behavior of these compounds in plasma environments commonly encountered in semiconductor fabrication processes. Through elucidating the various reaction pathways, our research endeavors to inform the design and optimization of gas precursors, ultimately facilitating the development of more efficient and environmentally sustainable semiconductor manufacturing technologies.

ALE-SuP-12 Plasma-Enhanced Atomic Layer Etching of Aluminum Oxide Using Trimethylaluminium and Nitrogen Trifluoride*, Ole Bieg, M. Kraut, T. Mikolajick,* Technische Universität Dresden, Institute of Semiconductors and Microsystems, Germany

While thermal atomic layer etching (ALE) processes using hydrogen fluoride (HF) and trimethylaluminum (TMA) have already been investigated [1][2], the critical nature of HF necessitates the explorations of alternative approaches. In this work, nitrogen trifluoride plasma (NF_3) is proposed as a replacement, offering improved handling characteristics as well as enhanced fluorination while maintaining the precision inherent in an ALE process. The investigation focuses on plasma-enhanced atomic layer etching (PEALE) of aluminum oxide (Al_2O_3) using NF_3 plasma and TMA.

This ALE process involves the fluorination of the Al_2O_3 surface by NF_3 plasma in the initial step, followed by the removal of the modified layer through a ligand exchange reaction in the second step using TMA. Experimental studies were conducted at temperatures ranging from 200°C to 300 °C, with a critical transition temperature observed at 250 °C, distinguishing between ALE of Al_2O_3 at high temperatures and atomic layer deposition (ALD) of AlF_3 at lower temperatures. The film growth at 200 °C indicates a shift in reaction mechanisms as a function of temperature.

The etch per cycle (EPC) showed a temperature-dependent saturation during TMA dosing and NF_3 plasma exposure. Etching of Al_2O_3 films was investigated with in–situ quartz crystal microbalance (QCM) measurements, a non-destructive measurement method for fast and accurate recording of saturation curves, which provides valuable insights into etching dynamics and process kinetics. In addition, an EPC of 1.4 Å/cyc was determined by in–situ spectroscopic ellipsometry (SE). The composition of the fluorinated Al_2O_3 layers as well as the composition after the removal step using TMA was determined using in–vacuo X-ray photoelectron spectroscopy (XPS).

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ALE-SuP-13 A Theoretical Study of Low Gwp Fluoro Gas Decomposition Properties*, Minji Kim, S. Lee,* Ewha Woman's University, Republic of Korea

Global warming is one of the serious problems about the earth's environment and the biggest cause of global warming is CO_2 released into the atmosphere, which has increased in concentration in proportion to the development of the industry, but other greenhouse gases such as perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) have also been shown to have a much stronger greenhouse effect than carbon dioxide. [1]

Because hydrofluorocarbons (HFCs) have a high infrared absorbency and long atmospheric lifetimes. The Global Warming Potentials (GWPs) which shows the degree to which other greenhouse gases contribute to global warming based on the impact of carbon dioxide on global warming, is 1,000 to 10,000 times as high as that of CO_2 (whose GWP is 1). CHF_3 molecule which is the simplest molecule among HFCs gases has 11,700 GWP index. [1]

These HFCs gases are used in various device-fabrication processes in the semiconductor industry, CHF_3 is used in the etching process of SiO_2 films. Since semiconductors are an indispensable part of modern technology. it is time to discover alternative gases with a low GWP index that can be used in the etching process.

Therefore C_3F_6O, one of the several Precursor gas candidates of fluoro-ketone, will be investigated for several radical species that decomposed during the etching process compared to the reference etching gas CHF_3, and will be calculation the energy of decomposition path by performing computation details of the quantum chemical calculations, Gaussian09 and density-functional theory (DFT) using the Vienna ab initio simulation package (VASP). [2]

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ALE-SuP-14 Enhancing Doping Efficiency in 2D Semiconductors using Cyclic Doping Method*, Ji Min Kim, J. Kang, H. Han, G. Yeom,* Sungkyunkwan University, Republic of Korea

Two-dimensional (2D) semiconductors, characterized by their thickness-dependent electrical and optical properties, are emerging as promising materials for future semiconductor technologies. The quest for improved properties in 2D materials involves strategies such as precise thickness management, large-scale production, and effective doping strategies. Doping, in particular, is essential for modulating the electrical behavior of 2D semiconductors, but conventional methods like ion implantation pose challenges, including potential damage to the delicate structures of nanometer-thick layers. In response, alternative surface treatment techniques such as plasma-based radical adsorption, liquid solution spin coating, and immersion have been explored. Nonetheless, these approaches, which predominantly modify the surface, tend to be less effective as the material's thickness increases. Addressing the need for better vertical doping uniformity, this research presents a novel cyclic doping technique using a layer transfer process. This method improves the efficiency of doping across multiple layers and preserves the distinct layered structure of MoS_2. The development of this cyclic doping strategy promises to overcome current limitations in doping efficiency and uniformity, marking a significant advancement in the manipulation of 2D materials for semiconductor applications with atomic layer precision.

ALE-SuP-15 Repairing Defects in Organosilane Self-Assembled Monolayers*, Yasuharu Miyamoto, Y. Yoshida,* SCREEN Holdings Co., Ltd., Japan*; T. Utsunomiya,* Kyoto University, Japan*; K. Sawada, S. Kunieda, Y. Ueda,* SCREEN Holdings Co., Ltd., Japan*; H. Sugimura,* Kyoto University, Japan

Area selective atomic layer deposition has been extensively investigated for advanced semiconductor device fabrication. Self-assembled monolayers (SAMs) are used as a protective layer for selective film deposition, and therefore, a defect-free monolayer is crucial for achieving high selectivity. Missing and misaligned precursor molecules can cause defects in SAMs [1]. Defect-free monolayers can be created by repairing defects, that is, removing the misaligned precursor molecules so-called physisorbed molecules, adding chemisorption sites on the surface and SAM reformation.

In this study, we assembled octadecyltrichlorosilane (ODTS) SAMs onto a SiO_2 substrate and applied intermediate wet cleaning solutions between multiple SAM formation processes. The wet cleaning solutions were selected from among various solvents with different values of the Hansen solubility parameter (HSP) to remove the physisorbed SAM's precursor molecules. We assumed that solvents with an HSP value closer to that of ODTS exhibits better solubility and removability of the physisorbed ODTS molecules. The SC-1 solution (ammonia and hydrogen peroxide mixture) widely used for the wet cleaning process to remove organic residue and to oxidize the surface was selected for adding functional groups on the surface of the defect area. The defects were analyzed using methods that combined post etching and AFM observation [2].

SAM formation with no intermediate wet cleaning, 1,3-bis(trifluoromethyl) benzene (high solubility of ODTS) and decane (low solubility of ODTS) resulted in 43.7 and 32.1 and 19.6 % of defect areas, respectively (Figure 1). These results indicated that wet cleaning effectively reduced the defects; however, no obvious correlation was observed with the HSP values. Toluene

combined with SC-1 solution reduced the defects area to 0.3 % (Figure 1). This result can be attributed to cleaning and the addition of a silanol functional group on the SiO_2 surface by a SC-1 solution, as reported by Hinckley et al. [1].

The combination of a solvent and an inorganic cleaning solution effectively repaired defects in ODTS SAMs, and a defect-free monolayer will be obtained by optimizing the cleaning solution.

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ALE-SuP-16 Damage-Free Plasma-Enhanced ALE of SiO_2, ***Daniil Shibanov**, D. Lopaev,* Lomonosov Moscow State University, Russian Federation; *Y. Zaseev, V. Varakin, D. Kostyukov,* JSC Research Institute of Precision Machine Manufacturing, Russian Federation; *A. Rakhimov,* Lomonosov Moscow State University, Russian Federation

The development of mechanisms and scenarios for plasma-enhanced atomic layer etching (PEALE) is of great importance for modern industrial technologies of nanostructures creation at the level of 2–7 nm on large wafers. The obvious criteria for the PEALE are high accuracy and repeatability of cycles, as well as the “damage-free” in the sense of complete absence of influence on the underlying layers of the material. In PEALE, as in other ALE technologies, this can be achieved by optimizing each step in the cycle.

This paper presents the optimization of PEALE SiO_2 (deposited from TEOS) in order to obtain highly reproducible and damage-free etching cycles. Typically, PEALE SiO_2 uses three basic steps in the cycle:

1) controlled plasma-enhanced deposition of a thin fluorocarbon CxFy layer of reagents;

2) ion activation of surface reactions;

3) removal of reaction products.

In this work, PEALE of SiO_2 was carried out in a 13.56 MHz ICP reactor for 200 mm wafers at low pressure (3Pa) with ion energy control by applying RF bias to a wafer. The reactor was equipped with in-situ laser ellipsometry for control over the dynamics of the surface layer of SiO_2. The plasma parameters were investigated by a Langmuir probe, a microwave hairpin probe, and an RFEA ion energy analyzer. To gain insight into material surface evolution, ex-situ XPS surface analysis was applied at each stage.

Optimization of PEALE SiO_2 was carried out by monitoring all three stages of the process by varying the parameters and structure of both the plasma itself and the composition of the mixture.

During the work, it was shown that highly reproducible (>100 cycles), homogeneous (<2% on a 200 mm wafer), damage-free PEALE of SiO_2 is possible in the following steps:

1) deposition of a C_xF_y film on a cooled wafer (-15 °C) at a constant, controlled rate in the downstream mode of an ICP discharge in an Ar/C_4F_8 mixture;

2) activation of surface reactions by Ar+ ions of optimal energy without removing the C_xF_y film in an Ar ICP discharge (with the application of an RF bias);

3) removal of reaction products with oxygen atoms and cleaning of reactor walls in the downstream ICP mode of discharge in an Ar/O_2 mixture (without applying RF bias).

The strategy of simultaneous control of the discharge structure (ICP mode) and plasma chemistry in PEALE steps allows for almost damage-free PEALE SiO_2.

ALE-SuP-17 Atomic Layer Etching of ITO, ***Christoffer Kauppinen,*** VTT Technical Research Centre of Finland

Indium tin oxide (ITO) is a degenerate n-type semiconductor often used as a transparent conductor. Oxide semiconductors like ITO are being studied for monolithic 3D integration on CMOS transistors, but to make ITO transistors with high on/off ratio the ITO channel needs to be thinned. This poster presents our recently published work of ITO ALE using thermal surface modification with BCl_3 and modified surface removal using Ar plasma. High synergy of 82% is obtained at 150°C. The etch per cycle (EPC) is 1.1 Å. The surface modification step exhibits excellent self-saturation and the modified surface removal step has a suitable self-saturation window. The ALE was developed in a conventional reactive ion etching (RIE) system. The developed ITO ALE was used to pattern ITO with conventional photoresist as the etch mask, and the etched areas are smoother than unetched areas, which is charasteristic of an ideal ALE process. The low-processing temperature, conventional photoresist compatible as etch mask, smoothening of the etched surfaces, and the use of conventional a RIE system make the ITO ALE process suitable for ITO transistor trials and fabrication.

ALE-SuP-18 Isotropic Atomic Layer Etching of Titanium Carbide Using Plasma-Exposure and Infrared Heating, ***Kazunori Shinoda,*** Hitachi High-Tech Corp., Japan; *T. Nguyen,* Nagoya University, Japan; *Y. Kozuma, K. Yokogawa, M. Izawa,* Hitachi High-Tech Corp., Japan; *K. Ishikawa, M. Hori,* Nagoya University, Japan

Isotropic atomic layer etching (ALE) is crucial for the advancement of the semiconductor industry, particularly due to the integration of three-dimensional high aspect-ratio structures in next generation devices. A notable method for achieving isotropic ALE is the plasma-assisted thermal cyclic ALE, which uses plasma exposure for the modification step and infrared heating for the desorption step. This method allows precise control over etching characteristics, such as material selectivity and surface roughness, by independently adjusting the temperatures for the modification and desorption steps. This control offers a high degree of tunability in etching parameters. A specialized 300-mm tool, namely dry chemical removal (DCR) apparatus, which comprises an inductively coupled plasma source and infrared lamps, has been developed to support this process. Over recent years, selective ALE of various materials, including Si_3N_4, SiO_2, TiN, W, and Co, has been demonstrated using the DCR apparatus. This paper presents the plasma-assisted thermal cyclic ALE of titanium carbide (TiC), commonly used in metal gate materials. To explore the etching mechanism, the experimental setup included a reaction chamber and *in-situ* X-ray photoelectron spectroscopy. Several TiC samples were exposed to radicals generated from the plasmas of fluorocarbon-based gas mixtures at a stage temperature of −20 °C. After plasma exposure, Ti 2p peaks indicating Ti–F bonds were observed, suggesting the formation of a titanium fluoride-based modified layer on the TiC surface. This modified layer desorbed from the TiC surface upon heating the samples at 100 °C, as evidenced by the disappearance of the Ti-F bond peaks. Cyclic etching tests were conducted by alternating between plasma exposure and infrared heating using the 300-mm DCR apparatus. The etching depth of TiC increased with the number of cycles, with an etched amount of 1.3 nm per cycle. The etching depth per cycle exhibited saturation behavior relative to the plasma-exposure time. Additionally, tests on stage temperature dependence revealed that self-limiting behavior was achieved only at a stage temperature as low as −20 °C, indicating that maintaining a low stage temperature is critical to prevent the desorption of reaction products during the surface modification step.

ALE-SuP-19 Atomic Layer Etching of Tantalum Nitride with Surface Fluorination Using Nf_3 or Cf_4 Plasmas, *H. Kang,* ***Minsung Jeon,*** *H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

A comparative study on atomic layer etching (ALE) process window was carried out for tantalum nitride (TaN) using nitrogen trifluoride (NF_3) and carbon tetrafluoride (CF_4) plasmas. The TaN surface was fluorinated with NF_3 or CF_4 plasmas and the fluorinated surface was subsequently removed by Ar ion sputtering. The chemical composition and bonding of the fluorinated layer were confirmed using x-ray photoelectron spectroscopy (XPS). The Ta-F_x bonds were identified in NF_3 plasma fluorination layer and Ta-F_x/Ta-C_x bonds were identified in CF_4 plasma fluorination layer. The depth of fluorinated layer was examined at various plasma exposure times using secondary ion mass spectrometry (SIMS). The fluorination depth reached a conversion depth of 8.4 nm for NF_3 plasma and 7.8 nm for CF_4 plasma. The depth of the fluorinated layer by NF_3 plasma was slightly deeper than that by CF_4 plasma at the same fluorination time.This result can be attributed to the Ta-C_x bonds on the surface, which inhibit the diffusion of fluorine (F) radicals. In the removal step, a wider ALE process window was observed at 50 – 90 V with NF_3 plasma compared to CF_4 plasma at 70 – 90 V. The difference in ALE ion energy window can be attributed to the difference in electronegative energy between Ta-F layer formed by NF_3 plasma and Ta-F_x/Ta-C_x layer formed by CF_4 plasma. The etch per cycle (EPC) of TaN was saturated at 180 sec of Ar ion sputtering for both NF_3 and CF_4 plasma. After the ALE process, the F residue remained at 5% on the TaN surface fluorinated with NF_3 plasma, whereas it was 3% in CF_4 plasma.

Atomic Layer Etching
Room Hall 3F - Session ALE-MoA
ALD+ALE and Emerging Topics in ALE

Moderators: Dr. Robert Clark, TEL Technology Center, America, LLC, Dr. Dmitry Suyatin, AlixLabs A.B.

4:00pm **ALE-MoA-11 Highly Selective Si Vertical Etching Enabled by Atomic-Level Process Utilizing $SiCl_4$ Plasma-Induced Selective Deposition***, **Miyako Matsui**,* Hitachi, Ltd., Japan*; M. Miura, K. Kuwahara,* Hitachi High-Tech Corp., Japan **INVITED**

Although the physical limitation of CMOS scaling is approaching, the local cell size of logic devices has still been continuously shrinking to improve the degree of integration. The patterning technology using extreme ultraviolet (EUV) lithography is one of key technologies for boosting pitch scaling. In addition, design technology co-optimization (DTCO) is another technology to boost cell size scaling, which enhances scaling by introducing various self-aligned processes. However, process challenges exist for both technologies. Etching processes using thin EUV resists, which needs to be thinner to accommodate the decrease in the depth of focus of EUV lithography, require extremely high selectivity and precise control of critical dimensions. Selective etchings for DTCO require high selectivity between layers having a similar material composition. In both cases, selective deposition for forming protective layers only on unetched materials can solve these process challenges and achieve extremely highly selective etchings.

In this study, we investigated a plasma-induced selective deposition process using a microwave-ECR etching system for forming a protective layer on top of the mask. A deposition layer was formed only on SiO_2 masks without forming an unnecessary deposition layer on Si surfaces of etching area, such as bottoms of the patterns and isolated etching area. This process effectively achieves extremely highly selective etchings by selectively forming the protective layers prior to the etching procedure in the same chamber.

We suggested a process for selectively forming protective layers on a SiO_2 without forming on a Si etching area by using a $SiCl_4/H_2/Cl_2$ plasma. On the Si surface, adsorbed $SiCl_x$ easily desorbed again by reacting with Cl generated from the plasma. On the other hand, adsorbed $SiCl_x$ on SiO_2 was thought to be more difficult to desorb by reacting with Cl due to Si-O having larger binding energy than Si-Si. After the deposition layer was selectively formed on the SiO_2 mask, the layer was oxidized using an O_2 plasma treatment to improve the etching resistance during the Si-etching. The O_2 plasma treatment time was controlled not to prevent the Si substrate from being etched during the Si-etching.

Finally, we demonstrated the selective deposition to etch a line-and-space pattern with a SiO_2 mask. In this process, selective deposition, oxidation, and Si etching were cyclically carried out. The extremely highly selective etching was achieved using the atomic-level selective deposition process without forming an unnecessary deposition on an isolated Si area.

4:30pm **ALE-MoA-13 Quasi-ALE Process Transfer from Lab to 300mm Line and Its Optimisation***, **Jenefa Kannan**, M. Rudolph,* Fraunhofer IPMS-CNT, Germany*; R. Jam, A. Karimi, D. Suyatin, J. Sundqvist,* AlixLabs, Sweden

Atomic layer etching (ALE) has found its place in advancing technologies as chip sizes continue to shrink and pitch sizes get smaller. The ALE process offers several advantages over conventional reactive ion etching (RIE) such as better directionality, uniformity, selectivity and damage free surface after etching [1,2]. A self-limited removal of material with minimal damage to the surface requires a good control over every step of the ALE process [3]. Quasi atomic layer etching (QALE) is defined as a process when more than one mono-layer of the material is etched per cycle. Surface treatment, Control of ion energies and appropriate evacuation of the chemical component (Cl_2) is necessary to control the etch rate per cycle and achieve etch saturation in a cycle sweep.

In our work, we have conducted in-depth studies to set up a molecular QALE process as seen in Figure 1 at our 300 mm facility in an inductively coupled plasma (ICP); decoupled plasma source (DPS) AMAT chamber on 350 nm amorphous Silicon (aSi) which was deposited on 12” blanket wafers. First, experiments were conducted to establish the bias power and pressure window. After this step, Ar sputter threshold for amorphous Silicon was determined. This was used as baseline to setup a cyclic process where the EPC was determined over low ion energies by optimising the bias power and activation time during exposure to Ar plasma. Damage or roughness caused to the layer being etched severely degrades device performance with decreasing dimensions [4]. Hence, to investigate the same, an Ellipsometer model was developed to understand the composition and thickness of this rough layer of the aSi surface post QALE etch. Thickness of the rough layer was evaluated over increasing number of cycles. The EPC for different Ar activation times at bias power 25 W is shown in Figure 2. The thickness of the rough layer at the end of the cycles is seen in Figure 3. We observed that the Ar activation time and no. of cycles have an influence on the thickness of the rough layer after etching.

In this work we investigate the factors and challenges that need to be taken into consideration while transferring the ALE process from lab to fab.In general, our work highlights the importance of control of every step in QALE for effective transfer and commercial viability in a 300mm line.

4:45pm **ALE-MoA-14 Deposition and Etchback Approach for Ultrathin ZrO_2 Coatings on TiO_2/ZrO_2 Core/Shell Nanoparticles***, J. Sempel, M. Kaariainen, T. Colleran,* University of Colorado at Boulder*; A. Lifschitz,* Meta Reality Labs*; **Steven George**,* University of Colorado at Boulder

Atomic layer deposition (ALD) and atomic layer etching (ALE) techniques were used to deposit and etchback a thin ZrO_2 shell on TiO_2/ZrO_2 core/shell nanoparticles. Possible pinholes in the initial ZrO_2 shell on the TiO_2/ZrO_2 core/shell nanoparticles were minimized by first growing thicker ZrO_2 films by ZrO_2 ALD. These thicker ZrO_2 ALD films were then etched back to produce thinner more continuous ZrO_2 films. The ALD and ALE were performed while the nanoparticles were agitated using a rotary reactor. ZrO_2 ALD films were deposited using sequential, self-limiting exposures of tetrakis(dimethylamino) zirconium (TDMAZ) and H_2O. Self-limiting conditions for the ZrO_2 ALD were determined by monitoring the pressure during multiple micropulses of the ALD reactants. *Ex situ* analysis of the nanoparticles was performed using transmission electron microscopy (TEM) to observe the growth of the ZrO_2 shell on the core/shell TiO_2/ZrO_2 nanoparticles. The ZrO_2 ALD led to more spherical ZrO_2 shells on the crystalline and more irregular TiO_2 cores in the absence of nanoparticle aggregation. The ZrO_2 ALD on the nanoparticles had a growth rate of 1.1 Å/cycle. Tunable ZrO_2 coatings were observed with thicknesses ranging from 5 nm to 25 nm after up to 250 ZrO_2 ALD cycles. The ZrO_2 deposited film was then etched back using sequential HF and $TiCl_4$ exposures. Self-limiting conditions for the ZrO_2 ALE were again determined by monitoring the pressure during multiple micropulses of the ALE reactants. Quadrupole mass spectrometry (QMS) experiments also identified $ZrCl_4$ etch products and TiF_xCl_y ligand-exchange products during the $TiCl_4$ exposures. *Ex situ* TEM studies revealed that the spherical ZrO_2 shells were maintained during the ZrO_2 ALE with no observable nanoparticle aggregation. The ZrO_2 ALE on the nanoparticles had an etch rate of 6.5 Å/cycle. Tunable ZrO_2 coatings were produced by the ZrO_2 ALE from 25 nm back down to 5 nm using 30 ZrO_2 ALE cycles. This procedure employing ZrO_2 ALD and ZrO_2 ALE provides exceptional control over the ZrO_2 shell thickness and quality on the TiO_2/ZrO_2 core/shell nanoparticles.

5:00pm **ALE-MoA-15 Study of Depositing Si_3N_4 on Si Wafers Using PEALD and Atomic Scale Removal of Underlying Native Oxide Using PAALE in the Same Chamber Without Ion Bombardment Damage***, **Birol Kuyel**, A. Alphonse, J. Alex,* Nano-Master

The mitigation of substrate damage is crucial to any process at the atomic scale (1). This is especially true for device technology applications in which source/drain and metalized regions are susceptible to damage (2). To eliminate substrate damage, we have developed plasma-enhanced atomic layer deposition (PEALD) of silicon nitride without ion bombardment (3).

The removal of native oxide on the Si wafer before depositing Si_3N_4 is also important for device performance (4). Removing the native oxides from the Si wafer using other means, such as reactive ion etching or wet etching, results in substrate damage and defects to the wafer.

Here, we will discuss the means of removing the native oxide from the Si wafer surface using Plasma Assisted Atomic Layer Etching (PAALE) prior to depositing silicon nitride. The PAALE process occurs in the same PEALD chamber, which prevents re-oxidation between steps. Furthermore, studies will be presented on the prevention of ion flux damage on the substrate surface with controlled ion energies and the possibility of performing PAALE without the incidence of any ions. The objective of the study is to develop a tool that can perform angstrom-precise PEALD and PAALE processes in the same chamber and prevent substrate damage.

References:

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3. US Patent # 9,972,501 B1 May 15, 2018
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5:15pm **ALE-MoA-16 N-Heterocyclic Carbenes for Area Selective Atomic Smoothing***, **Eden Goodwin**,* Carleton University, Canada*; M. Davies, P. Ragogna, M. Karttunen,* Western University, Canada*; S. Barry,* Carleton University, Canada*; C. Crudden,* Carbon To Metal Coating Institute / Queens University, Canada

High-volume manufacturing of microelectronics relies on thousands of sequential patterning, deposition, etch, and surface smoothing steps to create integrated circuits comprised of interwoven metallic, semiconducting, and dielectric features. Throughout the fabrication process, surface roughness is carefully monitored to ensure proper adhesion between layers and maximize distance between features. If surface roughness exceed tolerance limits, films are more likely to delaminate and manufactured features are more like to short-circuit.[1] At sub-nm feature sizes these tolerances become more challenging to reach.

Current smoothing techniques either rely upon top-down mechanical polishing[2] or on plasma methods.[3] Both techniques preferentially etch surface features, leaving a process gap for targeted surface smoothing on complex architectures. In pursuit of a more accessible smoothing methods compatible with complex architectures, we have identified a vapor phase method for smoothing gold surfaces using a known area selective small molecule inhibitor.[4] We explore the kinetics of adsorption and desorption of a N-heterocyclic carbene (NHC) through in-situ quartz crystal microbalance (QCM) analysis and molecular dynamics (MD) simulations. QCM traces (Fig. 1) show a saturative growth behavior for the initial dose of NHC achieving a surfactant density of 97 ng cm^{-2}, while subsequent doses saturate to 60 ng cm^{-2}. These differences are attributed to a reduction in the total number of available surface sites through atomic smoothing.

To confirm this, changes in surface roughness were analyzed through atomic force microscopy (AFM). AFM images (Fig.2) show a significant reduction in calculated root-mean-square (RMS) roughness values between surfaces left untreated (2.97 nm), heated under vacuum (2.38 nm) and those treated with NHC heated under vacuum (1.87 nm).

Atomic Layer Etching
Room Hall 3F - Session ALE1-TuM
ALE Applications and Methodologies

Moderators: Hannah Margavio, North Carolina State University, Prof. Dr. Fred Roozeboom, University of Twente and Carbyon B.V., The Netherlands

8:00am **ALE1-TuM-1 Current Status of ALE in Semiconductor Processes***, **Keun Hee Bai**,* Samsung Electronics Co., Republic of Korea **INVITED**

ALE process has been studied and used in the semiconductor processing for years.

There are a few benefits with the ALE, not only higher selectivity but also fine etch amount control or less loading.

In this presentation, we review the status of the ALE in the Fab for semiconductor manufacturing. What kinds of ALE and how much has it been adapted in the fab till now.

Considering the merits of the ALE, it has not been adapted widely. We will review the issues of the process in the line and what is necessary for more wide spread of the ALE.

8:30am **ALE1-TuM-3 ALE Preparation of Diamond Surfaces for Materials and Device Applications***, **Jeffrey Daulton**, M. Geis, M. Polking,* MIT Lincoln Laboratory

The expected high performance of ultrawide-bandgap semiconductors, resulting from the superior critical field, mobility, and thermal conductivity, has created substantial interest for their use electronics. Polishing of such substrates, however, has generally proven problematic, as the high bond energy that results in their wide bandgap also makes these materials relatively chemically-inert, limiting the effectiveness of CMP. Diamond, in particular, tends to form significant defects during the polishing process. As a consequence of the diamond sp^3 phase being metastable under standard conditions, these defects generally exhibit graphitic sp^2 bond character, making them readily etched in hydrogen plasmas. This results in even short exposures to hydrogen plasmas forming deep, crystallographically-etched pits in the polished surface. This has the effect of significantly limiting the quality of epitaxial growth on such surfaces, as diamond CVD growth inherently relies on initiation of the growth process with a hydrogen plasma. Such highlighting of defects also has negative implications for the mobility of diamond surface FETs, where the such a hydrogen plasma exposure is used to terminate the diamond surface and form a high-density 2-dimensional hole gas (2DHG) channel on the surface.

Smoothing by ALE has been demonstrated across a wide range of materials, suggesting the possibility for its use in pre-epitaxy surface preparation, provided near-surface plasma damage can be reduced sufficiently. Here, we use a Cl_2/Ar ALE cycle to prepare very smooth (Ra = 0.058 nm) diamond surfaces. Because of the tendency of damaged diamond to exhibit graphitic sp^2 bond hybridization, we use Raman spectroscopy, which is capable of differentiating between the diamond sp^3 peak and the graphitic sp^2 phase. This allows for observation of any reduction of near-surface damage with ICP etching or with ALE. Raman spectroscopy shows a clear reduction in sp^2 bonding with ALE from the ICP-etched surface, suggesting that this process removes the lattice damage induced by the ICP etching process. The remaining shallow, uniform sp^2 surface layer can then be easily removed during initiation of CVD growth to yield a high-quality growth interface.

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8:45am **ALE1-TuM-4 Comparison of Different PEALE Modes on AlGaN/GaN Heterostructures***, C. Miersch, **Sarah Seidel**,* Fraunhofer Institute for Integrated Systems and Device Technology IISB, Germany*; A. Schmid, J. Heitmann,* Department of Applied Physics, Technical University of Freiberg, Germany*; F. Beyer,* Fraunhofer Institute for Integrated Systems and Device Technology IISB, Germany

Nitrogen based group III-V compound semiconductors have become an integral part of consumer electronics and are essential for high-power and high-frequency applications. The Baliga's figure shows especially for GaN and AlN offer theoretically a high break down voltage (GaN: 5 MV/cm [1] and AlN: 15 MV/cm [2]) at low specific on-resistance [3,4]. Transistors based upon nitride semiconductors are high electron mobility transistors (HEMTs) and it can be realized by a heterojunction of an AlGaN barrier to a GaN buffer layer is forming two-dimensional electron gas (2DEG) [5,6], due to spontaneous and piezoelectric polarization. This normally-on transistors are desirable normally-off, which increases the safety for power-switching applications and suits to the established MOSFET circuit design. One way to shift the threshold voltage V_{th} in positive direction is to bring the gate contact closer to the channel by a precious and damage free recess etch of the AlGaN barrier (Fig. 1) [7]. This requires increasing demands on the manufacturing processes like dry etching to achieve smaller and high controllable etching rates, low damage, and minimized surface roughness. For this challenge atomic layer etching (ALE) is ideal. A conventional ALE approach on a AlGaN/GaN heterostructure could be described as followed. In the first step, the so-called modification step, the surface is modified by chlorine etching chemistry, producing a thin layer, ideally on an atomic scale, of volatile $GaCl_x$ and $AlCl_x$ products. In the second step, the so-called removal step, this thin layer can be easier removed then the unmodified surface below, by a physical impact of accelerated low energy Argon-ions. Typically purging in between the steps is applied, which increases the cycle time and affects the processing costs. An optimization of the cycle times and the implementation of other ALE methods can be beneficial.

For the experiments, a plasma enhanced ALE is used for etching. In this study, we develop an ALE recipe for the $Al_{25}Ga_{75}N$ barrier layer and optimized it in respect to the cycle times and the plasma damage. Furthermore, we compare different ALE methods: with purging in between the steps, purge-free [7], continuous plasma and a bias-pulsed [8] option. The evaluation of the developed processes will be performed by morphological and electrical characterization (gate recessed HEMTs). The induced damage will be investigated by structural and defect spectroscopical analysis.

9:00am **ALE1-TuM-5 Quasi-ALE Process for GaN: High Etching Rate Without Compromising the Surface Roughness***, P. Mouriño-Miñambres, R. Resta-López, F. Martin-Romero, **Miguel Sinusia Lozano**, V. Gómez,* Nanophotonics Technology Center - Universitat Politècnica de València, Spain

The atomic layer etching (ALE) process allows, theoretically, the selective atomic layer etching of the selected compound. In this work a Cl-based ALE process is developed to etch Ga-polar GaN (0001). Several parameters of the etching process are evaluated for assessing their influence on the ALE process namely, the ratio of the cycle devoted either to chlorination or Ar-sputtering and the applied RF power. The developed etching process, carried out at 5 mTorr, provides EPC values as high as 4 nm per cycle. Furthermore, because of the low-energy Ar plasma sputtering step, the etching process does not degrade the surface properties as reflected by the atomic force microscopy (AFM) and photoluminescence (PL) measurements without degrading the surface roughness [1]. Similar to other ALE processes reported in the literature, the smoothness of the surface is improved [2,3]. However, in comparison the EPC cycles in this work are larger-without any purge step within the cycle- thus reducing the time needed when the ALE process is applied during the nanofabrication process.

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9:15am **ALE1-TuM-6 A New Challenge for Developing Novel Atomic Layer Etching: Applying the Leidenfrost Effect to Obtain Floating Nanomist-Assisted Vapor Etching***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; Y. Yamaguchi, K. Shinoda,* Hitachi, Ltd., Japan*; K. Sun,* Nagoya University, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective etching of three-dimensional nanostructures in semiconductor devices requires a high-performance etching technology. In our previous

study, we developed a wet-dry etching or wet-like plasma etching that combines the advantages of wet etching (high isotropy and selectivity) and dry etching (high controllability) [1]. By using a high-density vapor plasma (wet-like plasma) at medium pressure, high-density reactive radicals are generated, significantly increasing the chemical reaction rate to the sample surface. This paves a new path for our development of the new dry atomic layer etching methods, named wet-like atomic layer etching (ALE).

Here we have proposed a new wet-like ALE method, named floating nanomist-assisted vapor ALE at relatively low temperature, that is aiming to minimize the damage from sputter effect in plasma ALE, high temperature treatment in thermal ALE during volatilization, and nanostructure damage in wet ALE. The phase with intermediate properties between mist liquid phase and vapor phase, named mist-vapor phase or nanomist phase that can maintain the wet properties of liquid phase at the minimal size less than 100 nm is proposed here for nanodevice applications. At the Leidenfrost point, the nanomist floats on its own stable vapor cushion film over the whole sample surface [2]. By using the Leidenfrost effect, the sample surface can be modified and/or etched by the floating nanomist-assisted vapor, this is an optimal condition to obtain an ultra-thin liquid-like layer in the shortest time. In the first step of cyclic process, the nanomist A is introduced and approaches the sample surface to form the floating nanomist A. Under the floating nanomist A, a stable vapor film A exists and reacts with the sample surface to form a modified layer. In the second step, the modified layer is removed by dissolving it in the highly volatile nanomist B flow, resulting in a clean surface and a controllable cyclic process.

An example of trying to apply the Leidenfrost effect to obtain floating nanomist-assisted vapor etching is demonstrated here for TiAlC film by using the H_2O_2 based mixtures at medium pressure. The nanomists of these liquid mixtures were generated by an originally developed atomizer that was controlled at room temperature. The highest etch rate of TiAlC film was obtained at the temperature of 175 ^oC that is considered as the Leidenfrost point of the nanomist produced from the aqueous liquid mixture, in which the TiAlC surface is supposed to be etched by the floating nanomist-assisted vapor.

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9:30am **ALE1-TuM-7 Electron-Enhanced Etching of Molybdenum Using Sequential O_2 and HCl Reactive Background Gases to Form Volatile Molybdenum Oxychlorides**, ***Michael Collings***, *S. George,* University of Colorado, Boulder

Molybdenum (Mo) is important for future back-end interconnects resulting from its favorable resistivity scaling as metal lines continue to shrink. Precision etching techniques are needed to fabricate these interconnects and clean the metal contacts. In this study, Mo etching was achieved utilizing O_2 and HCl reactive background gases (RBGs) in conjunction with low energy primary electrons at ~100 eV to create volatile Mo oxychloride products. The electrons can dissociate O_2 and HCl to generate ions or radicals. The electrons can also desorb surface species by electron stimulated desorption (ESD). In addition, the primary electrons at ~100 eV can form secondary electrons at lower energies. The primary electrons were obtained from a hollow cathode plasma electron source (HC-PES). The HC-PES is a chemically robust electron source that can deliver currents >200 mA over an area >10 cm^2.

Electron-enhanced etching was demonstrated on Mo films using sequential O_2 and HCl RBGs. Oxygen was dissociated by the electron beam and oxidized the Mo surface to form MoO_x. The Mo oxidization was dependent on the voltage potential on the substrate. In situ spectroscopic ellipsometry (SE) measurements of the MoO_x film thickness showed that Mo oxidation with a +20 V stage voltage was >7X faster compared with oxidation using a 0 V or -20 V stage voltage (Figure 1). We believe that the positive stage voltage can activate a new process mechanism involving secondary electrons (Figure 2). The attachment of secondary electrons to O_2 produces O_2 dissociation. O_2 dissociation creates negative O^- ions that are then attracted to the positive stage voltage. This mechanism explains the greatly enhanced oxidation rates with positive stage voltage.

Subsequently, the HCl RBG was dissociated by the electron beam to form chlorine species. The reaction of chlorine species with the MoO_x surface produces volatile MoO_xCl_y compounds. In situ SE measurements of the MoO_x film thickness monitored the etching of MoO_x by HCl RBG (Figure 3). The MoO_x etching was also dependent on the stage voltage. Low etching rates were observed at stage voltages ≤ +20V.Greatly enhanced etch rates were observed at stage voltages ≥ +30V. This enhancement is also attributed to secondary electrons that create Cl^- from the HCl RBG after dissociative electron attachment. Secondary electron emission from samples followed by electron attachment to form negative ions provides a new class of reactive species for etching. Positive stage voltages can be used to pull the negative ions to the substrate to enhance the etch rates.

9:45am **ALE1-TuM-8 Impact of Activation Strategies for Sio_2 Atomic Layer Etching Applied to Contact Patterning**, ***Antoine Ronco***, *F. Boulard, S. Lecré,* Univ. Grenoble Alpes, CEA, Leti, France*; N. Possème,* ST Microelectronics, France

The etching of SiO_2 for contact etching is classically carried out using continuous reactive ion etching (RIE). However, the development of novel architectures for advanced devices and applications often uncover new problematics. This motivates the refinement of etching techniques and processes, in order to etch high aspect ratio (HAR) features while maintaining very high values of selectivity to the underlying layer [1]. For this reason, Atomic Layer Etching (ALE) is receiving attention as it promises to enable a higher control of the process than RIE. In the case of SiO_2, to maintain throughput and etch HAR patterns, the contact etching process is carried out in a Capacitively Coupled Plasma (CCP) reactor. In these conditions, reaching ideal ALE is challenging for two reasons: the non-self-limited nature of the modification step, and the difficulty of obtaining an ideal activation step [2]. This way, developing processes that are free from variability such as aspect ratio dependent etching (ARDE) or intra-wafer non-uniformity is needed.

This work presents developments of Quasi ALE processes of SiO_2 and focuses on different strategies for the optimization of the activation step in order to increase the robustness of these processes.

Blanket and patterned samples are studied. Blanket samples consists of SiO_2 on Si wafers. Patterned samples consists of SiO_2 on SiN on Si wafers. These experiments are performed in a 300 mm FLEX FL CCP reactor from Lam Research. The modification step is carried out with a C_4F_6 / Ar plasma using the high frequency power generator. The activation step consists of an Ar plasma using the high and low frequency generators. The reactor is cleaned using an O_2 plasma before and after etching each wafer. Etch rates of SiO_2 and SiN are determined by ellipsometry and cross-section SEM.

The sputtering threshold of SiO_2 in low-pressure Ar plasma is investigated depending on the RF power used on the low and high frequency power generators. Conditions of ideal ALE activation in CCP and the implications on throughput are reported.

To limit ARDE and etch stop, alternative activation strategies are investigated through the addition of O_2 to the Ar activation plasma. The impact on pattern shape and SiO_2:SiN selectivity at the bottom of the contact is studied.

Finally, the implementation of a three-step cycle, with a deposition, activation and cleaning step, is investigated. The use of the cleaning step during each cycle or punctually after a certain amount of cycles is discussed, along with the development of said cleaning step.

[1] T. Bédécarrats et al., IEEE (IEDM), (2021).

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

Atomic Layer Etching
Room Hall 3F - Session ALE2-TuM

Thermal Gas-phase ALE

Moderators: Prof. Dr. Heeyeop Chae, Sungkyunkwan University (SKKU), Jean-François de Marneffe, IMEC

10:45am **ALE2-TuM-12 Thermal Etching of Metals and Metallic Materials for Gate-All-Around Devices**, ***Dimitri Kioussis***, *S. Karumuri, M. Uddin, S. Barnhill, Y. Huang, B. Erickson,* Intel Corporation **INVITED**

Isotropic Vapor Etch and Atomic Layer Etching (ALE) with extreme high selectivity have become essential technologies to continue Moore's law cadence for fabrication of next generation logic transistors beyond 2nm node. This talk reviews the status of Vapor Etch and ALE processes at Intel for etching various materials such as metals, metal nitrides, and metal oxides used across various sections of the process flow. The talk will outline basic thermodynamic principles and reaction kinetics as they apply to these reactions. Will discuss why in the nonsaturation mode etch anisotropies may occur that can lead to unwanted performance variations in high aspect ratio devices due to topological constraints imposed on the delivery of reactants and removal of reactant by-products. While ALE involves sequential modification of the etch surface followed by ligand exchange to

etch the material, thermal pseudo-ALE (Tp-ALE) uses thermal activation, instead of surface modification. Thereby, ligand exchange reacts with metal/metallic surfaces with or without surface modification. These two unique approaches offer atomic layer precision in removing metals/metallic films selective to other materials in the stack. This talk will briefly demonstrate the capability of ALE, Tp-ALE as well as combination approach in etch back, recess, and complete removal applications.

11:15am **ALE2-TuM-14 Low Temperature, Conversion-Free Thermal Atomic Layer Etching of Zinc Oxide using Hydrofluoric Acid and Trimethylgallium***, **Taewook Nam**, D. Zywotko, J. Partridge, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) processes have been developed based on various etching mechanisms. For example, metal oxides such as Al_2O_3, HfO_2, and ZrO_2 are etched based on "fluorination–ligand exchange" reactions. ALE studies have also shown that materials can be converted to a different material by reaction with the ALE precursors. The "conversion" based etching mechanism has been confirmed for ZnO ALE using hydrofluoric acid (HF) and trimethylaluminum (TMA). This study introduces a conversion-free thermal ZnO ALE using HF and trimethylgallium (TMG). ZnO thermal ALE using HF and TMG was studied using a variety of techniques including quartz crystal microbalance (QCM) and quadruple mass spectrometry (QMS). ZnO films were first deposited using atomic layer deposition (ALD) using diethylzinc (DEZ) and water (H_2O) at 100 °C. QCM measurements during ZnO ALE then observed digital mass gains during HF exposures and pronounced mass losses during TMG exposures. Under saturation conditions, the etch rates were 0.24, 0.52, 0.97, 1.35, 1.92, and 3.82 Å/cycle at 30, 60, 100, 150, 200, and 300 °C, respectively. One notable difference between ZnO ALE using HF/TMA or HF/TMG is that the etching can be achieved at 30 °C using HF/TMG, whereas ZnO ALE using HF/TMA requires temperatures ≥ 240 °C. To understand the temperature differences between the two chemistries, TMA and TMG were individually exposed to fresh ZnO ALD films. The mass after TMA exposure showed a pronounced decrease because of the conversion reaction. The TMA exposure converts ZnO to Al_2O_3. HF can then adsorb on the fluorinated Al_2O_3 surface. Subsequently, this HF can react with TMA to produce AlF_3 ALD at temperature < 240 °C. In contrast, the mass increased after TMG exposure on fresh ZnO ALD films because of TMG adsorption on the ZnO surface. HF then fluorinates ZnO to ZnF_2 and HF does not strongly adsorb on the ZnF_2 surface. Consequently, TMG does not react with HF to produce GaF_3 ALD. Because GaF_3 ALD does not compete with ZnO ALE, ZnO ALE can be performed at extremely low temperatures down to 30°C. QMS experiments were also performed to identify etch products during ZnO ALE using HF and TMG. The QMS experiments support the "fluorination-ligand exchange" reactions without conversion during ZnO ALE using HF/TMG.

11:30am **ALE2-TuM-15 Thermal Atomic Layer Etching of the Indium Gallium Zinc Oxide (IGZO) Family by Fluorination and Ligand-Substitution Hydrogen-Transfer Reactions***, **Troy Colleran**, J. Partridge, A. Abdulagatov, S. George,* University of Colorado at Boulder

Indium Gallium Zinc Oxide (IGZO) and its component metal oxides are important oxide semiconductors. Etching these metal oxides will be needed to fabricate thin channels for transistors. The thermal ALE of In_2O_3, Ga_2O_3, ZnO, and IGZO was achieved using sequential fluorination and ligand-substitution hydrogen-transfer (LSHT) reactions at 200°C. The two-step etching process was performed by first fluorinating the metal oxide using HF. Following fluorination, volatile release of the metal fluoride was accomplished using acetylacetone (Hacac). LSHT with Hacac leads to volatilization of the metals as stable, metal acetylacetonate compounds ($M(acac)_x$; M = In, Ga, Zn). During the LSHT reaction, acac from Hacac substitutes for fluorine in the metal fluoride. Hydrogen from Hacac also transfers to the metal fluoride to form HF. Etching of IGZO films was measured by *in situ* spectroscopic ellipsometry studies. IGZO etch rates of 0.3, 0.4 and 0.6 Å/cycle were measured at 200, 230 and 250°C, respectively, on IGZO thin films. Quadrupole mass spectrometry (QMS) studies also measured the etching of In_2O_3, Ga_2O_3 and ZnO powders at 200°C. In_2O_3 and Ga_2O_3 ALE were confirmed by the evolution of $In(acac)_3$ and $Ga(acac)_3$, as well as HF, during Hacac exposures after fluorination of the respective metal oxide. ZnO was found to be spontaneously etched by Hacac as evidenced by the continuous evolution of $Zn(acac)_2$ and H_2O during Hacac exposure despite no previous fluorination. Time-dependent studies of the etch products were also performed using QMS. The evolution of $M(acac)_x$ and HF during Hacac exposures on a previously fluorinated metal oxide was consistent with the proposed etch mechanism. The decay in $M(acac)_x$ signal intensity during Hacac exposures was evidence of self-limiting LSHT reactions. The spontaneous etching of ZnO using Hacac exposures did not prevent the thermal ALE of IGZO films.

11:45am **ALE2-TuM-16 Designing an ALE Process and Uncovering the Etching Mechanism for a 2D van Der Waals Material: Ternary Transition Metal Chalcogenide $CrPS_4$***, **Marissa Pina**, M. Whalen, J. Xiao, A. Teplyakov,* University of Delaware

$CrPS_4$ is a 2D van der Waals material in the ternary transition metal chalcogenide (TTMC) class of compounds. $CrPS_4$ is a semiconductor with A-type antiferromagnetic ordering, so thin flakes a few layers thick can display ferromagnetic or antiferromagnetic behavior depending on whether there is an odd or even number of layers.

In order to understand the magnetism down to the monolayer limit and their dynamic excitations in magnons and excitons, and make devices based on 2D magnetic materials viable for industry, 2D materials with well-controlled layer structures have to be produced. The existing methods for controlling $CrPS_4$ thickness, such as mechanical and liquid exfoliation, are either not well controlled or introduce damage to the crystal structure. In this study, we will show that thermal atomic layer etching (ALE) can be used to controllably etch the 2D crystals of this material without contaminating them. Ultimately, using ALE to manipulate the thicknesses of these flakes will allow for controlling their magnetic and dynamic optical properties.

$CrPS_4$ flakes were exfoliated onto a gold film from a single crystal via mechanical exfoliation. Thermal ALE cycles were performed in an ultra-high vacuum chamber. Each cycle consisted of a chlorine dose at elevated temperature using a solid-state electrochemical chlorine source, followed by an acetylacetone dose at elevated temperature. Atomic force microscopy was used to determine an average etching rate of 0.10 ± 0.07 nm/cycle. Although the etching rate appeared to depend on the thickness of the flakes, this average removal rate was recorded for 75 different points for flakes ranging from several nanometers to 90 nm in thickness. ALE also removed the island defects caused by exfoliation from the top of the flakes. XPS and ToF-SIMS were used to follow chemical changes in the material and to interrogate the distribution of etchant components within the flakes. The formation of chemical species containing acetylacetonate ligands was confirmed for all the components (Cr, P, S) of this TTMC, and the chlorination was followed in ToF-SIMS depth-profiling experiments. The ALE process that resulted in controlled material removal did not result in measurable surface contamination. Importantly, the etching of $CrPS_4$ is highly temperature-dependent, as lowering the process temperature by even 30 °C does not result in noticeable etching.

Atomic Layer Etching
Room Hall 3F - Session ALE1+AM-TuA

ALE & Sustainability

Moderators: Dr. Keun Hee Bai, Samsung Electronics Co., Ms. Leila Ghorbani, KU Leuven and Imec

1:30pm **ALE1+AM-TuA-1 Centering Sustainability in Future Plasma-Enhanced ALE Processes*, Nathan Marchack,*** IBM Research **INVITED**

Recent progress in the field of artificial intelligence has also highlighted the critical role of semiconductor manufacturing in delivering the necessary compute requirements. Simultaneously, the prospect of future proliferation of such technologies presents serious ramifications for the environment. Examinations of the increases in resource consumption as both software [1] and hardware [2] advance have raised awareness of the need to consider the sustainability of future development. In this talk we will examine this idea as it pertains to plasma-enhanced atomic layer etching (PE-ALE), building off our recent work on reducing gas usage in deep Si etching. [3] We review new results studying mechanisms of halogen substitution on Si surfaces and the need for synergy between all facets of the development process, from substrate materials to gas precursor development. Adopting this focus as soon as possible will strengthen the fundamental role of atomic layer processes in enabling future technologies.

[1] E. Strubel et al., Energy and Policy Considerations for Deep Learning in NLP, Proc. of the 57th Annual Meeting of the Association for Computational Linguistics, 2019, pp. 3645–3650, Florence, Italy.

[2] M.G. Bardon et al., DTCO including sustainability: Power-performance-area-cost-environmental score (PPACE) analysis for logic technologies, IEEE International Electron Devices Meeting (IEDM), 2020, pp. 41.4.1-41.4.4, San Francisco, CA, USA.

[3] O. Isowamwen et al., Characterization of TSV Etch from a Sustainability Standpoint, Proc. SPIE 12499, Advanced Etch Technology and Process Integration for Nanopatterning XII, 2023, 124990H, San Jose, CA, USA.

2:00pm **ALE1+AM-TuA-3 Life Cycle Assessment of GaN ALD*, Houyem Hafdi*,** *A. Carlson, H. Pedersen,* Linköping University, IFM, Sweden

ALD is a fast-growing industry; it is estimated to reach 6,2 Billion USD by 2028, which implies that the demand for metals and energy sources is increasing. Hence, the sustainability of ALD, other nanotechnologies, and nanomaterials has become a major concern and needs to be evaluated[1,2].

Life Cycle Assessment (LCA) is a process for evaluating possible benefits and different environmental impacts through a product´s life cycle based on the defined approaches of ISO 14044[3]and ISO 14040[4]. We will show how to apply the LCA methodology to examine and quantify the sustainability of ALD. We chose GaN as the model material for this study owing our experience of this process and of conventional CVD of GaN, allowing comparisons between conventional CVD and ALD. No research regarding LCA of GaN ALD has been carried out to date.

First, the standard LCA analysis is based on choosing a functional unit, which in our study is the deposition of a 20 nm GaN film from Triethygallium (TEG) and Ammonia (NH3) plasma on a 200nm-diameter silicon substrate. The second step is defining the system boundaries. We chose a cradle-to-gate system that investigates the life cycle phases throughout the entire ALD process. The third step is the inventory analysis where all inputs and outputs are collected, these data include material consumption, electric and thermal energy use, as well as air emissions and by-products. The LCA was carried out based on the Ecoinvent 3 database.

The final step is the impact life cycle assessment, where the results are then transformed into the impact categories of ecotoxicity (ET), global warming potential (GWP), human health (HH), ozone depletion (OD), resource fossil fuels (RFF), human toxicity cancer (HTC), and smog air (SA). We will discuss the sustainability of ALD of GaN from the LCA and pinpoint where the focus should be when making GaN ALD more sustainable.

1. Battisti, R.; Corrado, A. Evaluation of technical improvements of photovoltaic systems through life cycle assessment methodology. Energy 2005, 30, 952−967.
2. Pedersen, H., Barry, S. T., & Sundqvist, J. (2021). Green CVD—Toward a sustainable philosophy for thin film deposition by chemical vapor deposition. Journal of Vacuum Science & Technology A, 39(5)
3. ISO 14044; Environmental Management Life Cycle Assessment Requirements and Guidelines. International Standards Organization: Geneva, Switzerland, 2006.
4. ISO 14040; Environmental Management Life Cycle Assessment Principles and Framework. International Standards Organization: Geneva, Switzerland, 2006.

2:15pm **ALE1+AM-TuA-4 Specialization of Atomic Layer Etching to Address Sustainability Challenges*, Philippe BEZARD,*** IMEC, Belgium*; A. Fathzadeh,* KU LEUVEN, Belgium

Atomic Layer Etching (ALE) offers many attractive capabilities such as angstrom-level control over etch depth, excellent anisotropy (with plasma ALE) or isotropy (with thermal ALE), across wafer uniformity, and potentially lower damages than conventional plasma etching. However, in practice, it is rare to find an application where all those capabilities are needed at once and all the time. And thus, pure ALE is rarely found as a main etching process. In terms of sustainability, its extremely low throughput imposes the use of many more etch chambers than conventional processes to reach similar throughput, thereby multiplying consumption of process water, compressed air, power for the entire platform hosting the chambers (pumps, chillers, robots, etc.). Addressing the low throughput of ALE, without considering the type of gas used, is a major improvement for the environment. By only selecting the most relevant etching capabilities for a certain application, better trade-off between patterning performance and throughput can be achieved. Several approaches are tackling this issue such as quasi-ALE, Transient Assisted Plasma Etching, or by using ALE only as a corrective step to a faster sub-optimal etching process.

However, Atomic Layer Etching has several advantages which can be exploited to minimize the consumption of gases hostile to the environment (either by their Global Warming Potential or their toxicity/ corrosivity). First, by allowing enough time for the ions to desorb most etch products, the proportion of etchants adsorbed at the top surface that are used for the formation of a volatile product is high. Second, by removing purges and sacrificing full self-limitation, the outgassing of the reactor walls becomes a major supply of reactants. Cyclic processes such as ALE can be tuned for a better usage of the supplied gas than single-step processes. Finally, provided that enough etchant has been supplied to the entire wafer's surface, the excellent etch uniformity across wafer of ALE allows to run conditions maximizing gas usage which would otherwise be rejected in more conventional processes due to unacceptable compromises in uniformity. These unique properties can be exploited and have profound consequences on the design of the process chamber itself. This family of process should be considered as their own special category (not as a slightly different version of dry-etching), and have its own fully dedicated hardware in order to reduce their environmental impact.

2:30pm **ALE1+AM-TuA-5 Thermal Al_2O_3 Atomic Layer Etching Using HF and Hacac Reactants: Etch Enhancement from Refluorination by Product HF During Hacac Reaction*, Andrew S. Cavanagh,*** *T. Colleran, A. Abdulagatov, S. George,* University of Colorado at Boulder

Thermal ALE is typically defined by two sequential, reactant exposures separated by a purge. One reactant modifies the surface and the second reactant volatilizes the modified surface layer. In this study, a new ALE reaction process was identified where the surface modification reactant is also a reaction product of the volatilization reaction. Under these circumstances, etching can continue nearly indefinitely by repeating the exposure of the volatilization reactant. This study explores Al_2O_3 ALE using HF as the surface modification reactant and Hacac as the volatilization reactant. The reactions were monitored *in situ* using quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS). HF fluorinates the Al_2O_3 surface to AlF_3 in the first reaction and then Hacac volatilizes the AlF_3 surface layer forming $Al(acac)_3$ and HF in the second reaction. The HF reaction product from the Hacac reaction can then serve as a surface modification reactant to refluorinate the Al_2O_3. By performing multiple mini-doses of Hacac after an initial HF exposure, a large etch rate enhancement is observed for Al_2O_3 ALE compared with a single Hacac mini-dose. Figure 1 displays the QCM response to 10 Hacac mini-doses at 250 °C. Each Hacac mini-dose results in a net mass loss. The first Hacac dose removes the most mass. The 10th Hacac dose removes the least mass. The diminishing returns with subsequent Hacac mini-doses are the result of loss of some HF reaction product to the gas phase. If all the HF were recycled, then the HF reaction product could lead to perpetual etching. Similarly, Figure 2 shows the QMS response for successive Hacac mini-doses on HF-exposed Al_2O_3 at 250 °C. All QMS signals show a diminished response with successive Hacac exposures. The HF^+ signal is evidence of HF produced during the volatilization step that escapes to the gas phase. The H_2O^+ signal

is consistent with surface refluorination by HF reaction product. The $Al(acac)_2^+$ and $Al(acac)_3^+$ signals result from volatilization of the AlF_3 surface layer. The diminishing response is attributed to the loss of HF to the gas phase. With ten Hacac mini-doses per cycle, Al_2O_3 etch rates were determined using QCM between 160 – 300 °C. The largest etch rate of 3.07 Å/cycle [91.0 ng/(cm^2·cycle)] was observed at 290 °C. The smallest etch rate of 0.04 Å/cycle [1.1 ng/(cm^2·cycle)] was measured at 160 °C.

2:45pm **ALE1+AM-TuA-6 Elucidating Gas Phase and Surface Reactions of Atomic Layer Etching*, Taylor G. Smith,*** University of California, Los Angeles*; E. Crumlin,* Lawrence Berkeley National Laboratory*; J. Chang,* University of California, Los Angeles

Atomic layer etching (ALE) is playing an increasingly important role in the manufacturing of nanoelectronics and other devices. Theoretical calculations are often used to screen for viable ALE processes by predicting thermodynamically favorable etch products. However, experimental verification of the predicted etch products is needed. In this work, magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) and ambient pressure X-ray photoelectron spectroscopy (AP-XPS) are explored as methods to study ALE mechanisms in the gas phase and at the surface.

Recent advances in MAS-NMR rotor design have enabled the study of heterogenous systems, and this work builds on these advances to study the vapor-solid interactions that lead to etching in thermal ALE processes[1]. A novel MAS-NMR rotor packing method is discussed that is adapted specifically to the study of vapor solid interactions that are the backbone of thermal ALE. This method allows for segregation of a liquid etchant from the solid at room temperature, but exposes the solid to vapor phase etchant when the rotor is heated. MAS-NMR is then used to study the thermal ALE mechanisms of a CuO system etched in ^{13}C-enriched formic acid vapor, with the results indicating a dimeric product with antiferromagnetically coupled Cu centers, in agreement with predicted results. AP-XPS, in turn, can be used to look specifically at surfaces during thermal reactions. Again, CuO in formic acid is used as a model system to demonstrate the applicability of this technique.

[1] A. Chamas, L. Qi, H.S. Mehta, J.A. Sears, S.L. Scott, E.D. Walter, D.W. Hoyt, *Magn. Reason. Imag.***56**, 37 (2019).

3:00pm **ALE1+AM-TuA-7 Thermal Atomic Layer Etching of Ta with $NbCl_5$ and O_2*, Juha Ojala,*** *M. Chundak, M. Vehkamäki, A. Vihervaara, M. Ritala,* University of Helsinki, Finland

The widely used Cu interconnects in integrated circuits require diffusion barriers to prevent the diffusion of Cu into dielectric layers and contamination of Cu by the constituents of the dielectric layers. Materials used for this barrier layer include TiN, TaN and Ta metal. Processing these materials in a controllable manner becomes critical as the interconnects and barrier layers need to shrink to accommodate the smaller feature sizes in future integrated circuits. Atomic layer etching (ALE) is one such controllable method, which can be used to thin deposited layers, selectively etch unmasked areas of films, and to remove unwanted deposits in additive manufacturing methods, e.g., as a corrective step in area-selective deposition.

We present an isotropic ALE process for etching metallic Ta, based on oxidation of the surface layer with O_2 and etching of the resulting oxide with $NbCl_5$. The ALE process was studied using XRR and EDS thickness measurements as well as with XPS studies. The films were characterized before and after etching using XRD, EDS, SEM, and AFM. Effect of the film crystallinity on the etching process was studied in detail, along with oxidation of the films during etching.

Etching was studied at 300–400 °C using Ta films consisting of a mixture of cubic α-Ta and tetragonal β-Ta, as well as films consisting solely of α-Ta. It was found that the β-phase of Ta etches much more readily and is also prone to etching with $NbCl_5$ even without the oxidizer. Etch per cycle (EPC) of at least 2.0 and 4.0 Å was found for etching α-Ta at 300 and 350 °C, respectively. Gas phase etching of Ta_2O_5 and other oxides with $NbCl_5$ was also studied.

Dissolution of oxygen into the Ta films during etching was evident, and even a suboxide phase was observed during prolonged experiments. Otherwise, partially etched films were free of impurities. The mixed phase films showed development of island-like morphology due to the different EPC of the two phases, whereas the α-Ta films etched uniformly and had smooth surfaces. This study shows that thermal ALE of Ta is simple to perform in principle, but the phase composition of the metal can have significant effect on etching characteristics.

3:15pm **ALE1+AM-TuA-8 Atomic Layer Etching of Tantalum: Unlocking the Etching Mechanism by in-Vacuo XPS Studies*, Mykhailo Chundak,*** *J. Ojala, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Atomic layer etching (ALE) has emerged as a promising tool/method for nanofabrication technologies, offering the incomparable precision and control in material removal processes. The etching mechanism involves a set of self-limiting surface reactions that achieve the atomic-scale precision, uniform etching and volatilization of the modified surface. The reaction mechanism depends on the varieties of factors like chemical energy, kinetic energy etc. To elucidate the mechanisms of the reactions we used the cluster tool setup in HelsinkiALD laboratory[1]. The tool allows us to study the reactions with surface science techniques in vacuo after interrupting the reactions at each pivotal step giving us new insights about the reaction intermediates and thereby processes occurring at the surface.

Here we present results of the etching process of tantalum metal thin films. Tantalum, renowned for its exceptional corrosion resistance, holds significant importance across various industries, including microelectronics, catalysis, and energy storage. The 40 nm thick Ta films were first deposited via filtered cathodic arc discharge (FCAD) and subsequently subjected to an intricate etching process at 300 °C with $NbCl_5$ and O_2 within the cluster tool. Stoichiometry of the films was studied by X-ray photoelectron spectroscopy (XPS) at each step of the etch process. Initially the tantalum films were subjected to sputtering using Ar^+ ions to effectively remove the oxide layer, ensuring a pristine surface for subsequent reactions. Following this, controlled oxidation with O_2 gas was implemented to form surface oxides on the tantalum films. Finally, the tantalum films were exposed to $NbCl_5$, allowing for the observation of chemical composition changes indicative of the etching process. Notably, the etchant effectively removes the tantalum oxide layers starting from the highest oxidation states until the lower ones resulting in the stoichiometry reminiscent of the surface after sputtering.

Through systematic investigation and analysis, this study provides insights into the complex dynamics of atomic layer etching applied to the Ta thin films. The findings contribute to a better understanding of the ALE processes and valuable insights into precise control of the materials modification for further technological applications.

(1) Nieminen, H.-E.; Chundak, M.; Heikkilä, M. J.; Kärkkäinen, P. R.; Vehkamäki, M.; Putkonen, M.; Ritala, M. In vacuo cluster tool for studying reaction mechanisms in atomic layer deposition and atomic layer etching processes. *Journal of Vacuum Science & Technology A* **2023**, *41* (2). DOI: 10.1116/6.0002312 (acccessed 1/30/2024).

Atomic Layer Etching
Room Hall 3F - Session ALE2+AM-TuA

A.I. for ALD and ALE, and Wet-Chemical ALE

Moderators: Eric Liu, Tokyo Electron America, USA, Dr. Kazunori Shinoda, Hitachi, Ltd.

4:00pm **ALE2+AM-TuA-11 Application of Machine Learning to Atomic-Scale Process Development*, Satoshi Hamaguchi,*** Osaka University, Japan **INVITED**

For the development of new atomic-scale processing such as atomic layer etching (ALE) and atomic-layer deposition (ALD), efficient selection of precursor gases and other process conditions is desired among a large number of possible combinations of them. Artificial intelligence (AI) and machine learning (ML) techniques are expected to facilitate this selection. In this presentation, after briefly reviewing recent developments in data-driven plasma science [1] for process development and control in general,we discuss a method to predict the sputtering yields/etch rates of materials by ion impact based on experimental and simulation data of sputtering yields/etch rates. In such predictions, the sputtering yield typically depends on a relatively small number of physical parameters that characterize the surface material and incident ions (such as the masses of the surface material atoms and incident ions). However, the availability of large sputtering yield data is crucial for accurate prediction. Because experimental data for specific material and ion combinations may not be available, physics-based numerical simulations can be used to augment these data. For example, classical molecular dynamics (MD) simulations can be used to provide sputtering yield data but interatomic force-field models for “unfamiliar” materials are often of questionable accuracy. A method to develop ML-based interatomic force-field models is presented with an example of Si etching, and the challenges of such methods for general materials are discussed.

[1]R. Anirudh, et al., "2022 Review of Data-Driven Plasma Science" IEEE Trans. Plasma Sci. 51(7) 1750-1838 (2023).

4:30pm **ALE2+AM-TuA-13 Surrogate Models for One-Shot ALD and ALE Process Transfer Across Reactors and High Aspect Ratio Substrates*, Angel Yanguas-Gil*,** *J. Elam,* Argonne National Laboratory

Being able to predict the behavior of ALD or ALE processes when transferred from a lab setting to manufacturing would help accelerate the adoption of ALD and ALE in a wide range of applications, from energy materials to microelectronics. Current approaches require extensive tool time and characterization or, when assisted by simulations, accurate models carefully tuned to each specific process. In addition to reducing the risk and cost of adopting new processes, being able to predict the behavior of a specific precursor across reactors and types of substrates can also be used to discriminate processes that struggle to perform well under more challenging conditions present in manufacturing. A key challenge is our lack of information about many ALD and ALE processes. This includes not only the surface kinetics, but in many cases the precursor pressure in the reactor or upstream precursor consumption. It is therefore key to understand how can we compensate for this lack of information with more readily available experimental data.

In this work, we tackle this problem from a machine learning perspective. In particular, we have focused on using surrogate models as tools to help us understand the following two questions: 1) how can we predict process performance across reactors and substrates?; 2) what are the key experimental observables that we need in order to make such connection? Building on our prior work on artificial neural networks for ALD process optimization,[1] we constructed surrogate models trying to connect experimental data under lab conditions with key process metrics relevant for manufacturing. These include predicting throughput, precursor utilization, process variability across large area substrates, or expected conformality. These models are built using datasets from simulations that have been shown to agree well with experimental data for a few known processes, such as Al_2O_3 growth from trimethylaluminum and water.[2] Our results show that a careful experimental design involving the characterization of film thickness at predefined reactor conditions under undersaturated conditions is often enough to compensate for the lack of knowledge of a specific process. The downside is that the surrogate models are dependent on the specific reactor geometry. However, within a given reactor, surrogate models show predictive behavior across a wide range of surface kinetics and precursor pressures as long as the process kinetics is represented in the training set.

[1] A. Yanguas-Gil and J. W. Elam, *J. Vac. Sci. Technol. A* 40, 062408 (2022)

[2] A. Yanguas-Gil, J. A. Libera and J. W. Elam, *J. Vac. Sci. Technol. A* 39, 062404 (2021)

4:45pm **ALE2+AM-TuA-14 Ligand-Assisted Surface Layer Formation in Wet Atomic Layer Etching of Molybdenum*, Tulashi Dahal*,** *K. Abel,* Tokyo Electron America Inc.*; N. Levtchin,* TEL Manufacturing and Engineering of America, Inc.*; T. Hurd,* Tokyo Electron America Inc.,*; A. Rotondaro,* Tokyo Electron America Inc.

There are many applications for molybdenum in the semiconductor industry including metallization in logic BEOL and 3-D NAND. These applications often require partial etch back where the post-etch morphology is critical to device performance. Wet atomic layer etching (ALE) offers materials removal with Angstrom-level precision following two sequential, self-limiting, wet processing steps. In the first step, a Mo surface is exposed to an oxidizing solution that forms a self-limiting oxidation layer. In the second step, this layer is selectively dissolved in a second solution. Formation of a self-limiting Mo oxidation layer is challenging due to the solubility of molybdenum oxides in aqueous solution, which leads to continuous Mo etch and rougher post-etch morphology. Solubilization of Mo oxides can be delayed in a non-aqueous oxidizing solution. Mo surface oxidation in non-aqueous solution is, however, not self-limiting (Fig. 1). The post-etch morphology of Mo in cyclic etch experiment using non-aqueous oxidizing solution is rougher compared to the starting coupon owing to preferential grain boundary etching. Here we present our results on improving the self-limiting nature of Mo oxidation layer by adding a ligand to the oxidizing solution. Aqueous oxidation of Mo leads to a continuous etch, non-aqueous oxidation leads to a delayed etch, but adding a ligand to the oxidation solution leads to the formation of a stable passivation layer (Fig. 1). Cyclic etch experiments were carried out to estimate the Mo etch rate by exposing the Mo coupon in non-aqueous solution with and without a ligand. The drop in Mo ER from ~0.10 nm/cycle to ~0.07 nm/cycle after adding millimolar amount of ligand in the oxidizing solution indicates the changes in surface chemistry with ligand (Fig. 2). The dissolution of modified layer can be significantly increased via enhanced dissolution kinetics at an elevated temperature nearly doubling the Mo etch rate (~0.12 nm/cycle). Mo ER (~0.12 nm/cycle) is constant from 5 mM to 100 mM of ligand and drops to ~0.08 nm/cycle for higher ligand concentration remaining constant thereafter. The drop in Mo etch rate with higher ligand concentration may be attributed to the piling up of surface products that are less soluble in the dissolution chemistry B. The measured RMS roughness and the SEM images (Fig. 3 and inset) show that addition of a ligand decreases the post-etch surface roughness to the level of the unetched reference coupon. We attribute these differences in etch rate and post-etch morphology to improvements in the conformality and self-limiting nature of the surface oxidation layer with the addition of a ligand.

5:00pm **ALE2+AM-TuA-15 Wet Atomic Layer Etching of Ruthenium*, Kate Abel*,** Tokyo Electron America, Inc.

We have developed a new process chemistry for atomic layer etching (ALE) of ruthenium (Ru) using wet chemistry at room temperature. Unlike plasma- and thermal-ALE, material removal in wet ALE is achieved through selective dissolution of a self-limiting passivation layer rather than volatilization. In wet ALE, a self-limiting surface layer is chemically formed upon exposure to the first etching solution. The surface layer must be insoluble in this solution, but readily soluble in the second etching solution in order to complete the ALE cycle. The dissolution of the surface layer in the second solution mayoccur either through intrinsic solubility of the modified layer or through a selective reactive dissolution process. Additionally, the second solution must be unreactive with the freshly exposed metal surface. Sequential exposure to both etchants is therefore required for material removal. A diagram of this process is shown in Figure 1.

Forming a self-limiting layer on Ru that is capable of being selectively solubilized in a second solution is challenging. The common oxides, RuO_2 and RuO_4, are unsuitable – RuO_2 requires harsh, non-selective chemicals to be removed and the low melting point, volatility, and high solubility of RuO_4 prevent the formation of a stable passivation layer. Many non-oxide Ru compounds are known. Synthesis from the metallic state, however, generally requires oxidation to less stable intermediate oxidation states.

In this talk, we show that self-limiting passivation of the Ru surface can be accomplished by controlling both the oxidation potential and co-reactants present in solution. We pair an oxidizer with a variety of co-reactants in solution to show that the chemistry at the Ru surface can be changed from a continuous dissolution process to the formation of a self-limiting surface layer by changing the identity of the co-reactant. In the self-limiting case, completion of the wet ALE cycle can be accomplished through reactive dissolution of the Ru surface layer in a second etching solution. We present quartz crystal microbalance data to show how the oxidation conditions, co-reactant identity, and dissolution conditions influence the behavior of the Ru surface in this cyclic etch process.

5:15pm **ALE2+AM-TuA-16 Combined Dry-Wet ALE for Tungsten: A Surface Characterization Study*, Cinzia Chan*,** KULeuven, Imec, Italy*; J. de Marneffe,* IMEC, Belgium*; C. Gort,* TU Darmstadt, Germany*; J. Serron, M. Agati,* IMEC, Belgium*; J. Hofmann,* TU Darmstadt, Germany*; S. De Gendt,* KULeuven, Imec, Belgium*; D. van Dorp,* IMEC, Belgium

The continuous device scaling towards atomic-scale dimensions is facing challenges due to increasing complexity at both architecture and structure level. At these scales, the requirements for etching processes are limited to angstrom level. Therefore, atomic layer etching (ALE) and cleaning (ALC) are currently extensively studied as they utilize self-limiting reactions to etch surfaces with high control.

Tungsten is a material of high interest as it is currently being explored for MRAM and spintronic applications[1,2]. The reported ALE processes are halogen-based plasma[3,4] and often require high temperatures (>200˚C) to form volatile byproducts[5,6]. However, limitations on the thermal budget and the use of plasma processes may be incompatible or detrimental to the exposed materials in the device stack. Therefore, we propose a combined dry-wet ALE approach that consists of a self-limiting oxidation step (dry) combined with a selective oxide removal step in acidic solution. The advantage of a selective wet etch is that it does not induce any physical or structural damage (e.g. amorphization) as compared to a full dry approach.

The proposed dry-wet ALE method was investigated on W blanket layers and patterned structures. Surface oxidation was performed through an O_2

plasma treatment at 60˚C, followed by oxide product removal in dilute HCl solution at RT. Inductively coupled plasma mass spectrometry (ICP-MS) was used to study oxide etching kinetics and selectivity by quantification of the etched surface density of W in time. During the first minutes a rapid removal of W oxide was observed followed by a gradual lowering of the etched surface density towards a constant level that corresponds to the background etch rate of the metal. An oxide/metal etch selectivity of ~100 was found. Selectivity could be further improved by lowering the dissolved O_2 concentration in the etchant. While ICP-MS quantification and TEM inspection revealed that the bulk of the oxide is removed within 20 minutes, post-operando XPS measurements confirmed that a remaining interfacial (sub)oxide monolayer was only removed after 60 minutes of immersion in the acid. Conductive AFM measurements agreed with these observations. The etch per cycle was 0.8nm/cycle while the surface morphology was maintained.

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Atomic Layer Etching
Room Hall 3F - Session ALE1-WeM
Plasma and Energy-Enhanced ALE

Moderators: Dr. Dmitri Kioussis, Intel Corporation, Prof. Christophe Vallée, University of Albany

8:00am **ALE1-WeM-1 Anisotropic and Isotropic Plasma-Enhanced Atomic Layer Etching Processes for Metals and Dielectric Materials for Semiconductor Devices*, Heeyeop Chae,*** Sungkyunkwan University (SKKU), Republic of Korea **INVITED**

The critical dimensions of semiconductor devices are continuously shrinking with 3D device structure and are approaching to nanometer scale. The demand for dimension control in angstrom level is drastically increasing also in etching processes. In this talk, various plasma-enhanced ALE (PEALE) processes are discussed for anisotropic and isotropic patterning of metals and dielectric materials including molybdenum, ruthenium, cobalt, titanium nitride, tantalum nitride, aluminum oxide, hafnium oxide, zirconium oxides, silicon oxide, and silicon nitride. [1-10] Typical ALE processes consist of surface modification step and removal step. Various surface modification schemes were applied including fluorocarbon deposition on surface, surface fluorination, surface chlorination, surface oxidation with radicals generated with plasmas. For the removal or etching step, the modified layers were removed by ion-bombardment, heating, ligand exchange, ligand volatilization, or halogenation. The characteristics of reaction kinetics, surface roughness, surface residue in the plasma-enhanced ALE processes will be also discussed.

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8:30am **ALE1-WeM-3 Plasma Atomic Layer Etching of Titanium Nitride with Surface Fluorination or Chlorination and Ar Ion Bombardment*, Heeju Ha*,** *H. Lee, M. Jeon, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Plasma atomic layer etching (ALE) processes were developed for titanium nitride (TiN) with surface fluorination or chlorination in the modification step and ion bombardment in the removal step. In the modification step, the TiN surface was fluorinated using NF_3 plasma to form Ti-F bonds or chlorinated using BCl_3 plasma to form Ti-Cl bonds. The fluorinated or chlorinated layers were removed by ion bombardment using Ar plasma. The etch per cycle (EPC) of TiN was investigated depending on ion energy and etching time. The ALE window of constant EPC of TiN was confirmed in the energy range of 25 – 80 V for fluorination and 70 – 80 V for chlorination. The EPC of TiN was determined to be 1.5 nm/cycle in fluorination and 3.8 nm/cycle in chlorination in the ALE window region. The EPC of TiN increased with increasing Ar plasma time and exhibits self-limiting properties at 180 seconds for both fluorination and chlorination. The strong Ti-F peak was observed about 13% on the surface after ALE process with fluorination, but small Ti-Cl peaks were observed below 1% after ALE process with chlorination. The Root-mean-square (RMS) roughness of the TiN surface after ALE was measured at 0.24 nm for fluorination and 0.29 nm for chlorination, which is lower than before etching.

8:45am **ALE1-WeM-4 Isotropic Plasma Atomic Layer Etching of Nickel Aluminide Binary Intermetallic Using a Super-Cycle Sequence Based on Hhfac and Al(CH_3)$_3$*, Ali Mohamed Ali,*** IMEC Belgium*; G. Krieger,* TU / Eindhoven, Netherlands*; J. Soulié, C. Pashartis,* IMEC Belgium*; C. Detavernier,* Ghent University, Belgium*; H. C. M. Knoops, E. Kessels,* TU / Eindhoven, Netherlands*; S. De-Gendt, F. Lazzarino, S. Kundu, J. de Marneffe,* IMEC Belgium

Nickel aluminides have attracted tremendous research attention as a potential alternative material for barrier-less interconnects and EUV mask absorber applications due to its lower resistivity than other elemental metals and higher printing resolution, respectively.[1,2] However, down-scaling these binary intermetallics brings emerging challenges in developing etch methods due to the high chemical inertness and low gas-phase volatility of Ni compounds. In addition, preserving the concentration of each element in the alloy during the etching process is essential to be useable at the nanoscale. In this work, we report a new and promising approach towards the atomic layer etching (ALE) of stoichiometric NiAl and Ni_3Al. A super-cycle ALE process has been developed, in which each sub-cycle enables the removal of the Al-rich and Ni-rich phases, respectively. Fluorine-containing plasma and trimethyl-aluminum (TMA) precursors have been utilized to etch Al in the first phase. Whereas, in the second phase, the etching of Ni has been achieved using a nitrogen-containing plasma, probably forming Ni nitride and then chelation by hexafluoro-acetylacetone (Hhfac) precursor. A fundamental ALE study on each individual ALE process has been performed on pure Ni and pure Al films to evaluate the etching efficiency and selectivity of each element versus the other. *In-situ* spectroscopic ellipsometry measurements were employed to elucidate the self-limiting nature of the ALE sequence on the pure metal film and thickness change during alloy etching. The saturation behavior for each precursor on the compatible pure metal films has been observed. X-ray reflectivity measurements were carried out to confirm the etch rates on Ni-aluminide films. The etch rates were varied from 0.5 ± 0.10 Å/super-cycle at 250 ˚C to 3.3 ± 0.23 Å/super-cycle at 350 ˚C. Furthermore, atomic force microscopy analysis shows that thin Ni aluminide films remained smooth during initial etching and might introduce a little roughness when the etch cycles progressed. The results obtained from x-ray photoelectron spectroscopy confirmed that, at the optimized super-cycle ALE process, the etched Ni aluminide films still preserve the same concentration of each element in the alloy. The developed ALE process enabled the etching of nickel aluminide alloys and created a paradigm for future studies on alternative etching of binary intermetallics.

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[2] Luong, Vu, et.al.“*Ni-Al alloys as alternative EUV mask absorber.*”Applied Sciences 8.4(2018):521.

9:00am **ALE1-WeM-5 Surface Effects in Quasi-ALE of Si: A Correlation with Ar^+ Ion Energy**, *O. Danielsson,* Lund University, Sweden*; A. Karimi, M. Asif,* AlixLabs AB, Sweden*; S. Khan,* Danish Fundamental Metrology Institute, Denmark*;* ***Ivan Maximov,*** Lund University, Sweden

Atomic Layer Etching (ALE) is a self-limiting process used in nanofabrication that allows for precise material removal on the atomic scale by a cyclic nature introducing reactive gas adsorption and removal of surface atoms by a low-energy ion bombardment. In practical realisation of ALE, e.g. using commercially available RIE tools, the ion energy in plasma may exceed the sputtering threshold, typically 20-40 eV. It will result in a quasi-ALE (Q-ALE) regime where the process steps are not self-limiting, but still highly accurate and of lower damage compared to RIE. Direct measurements of the ion energy in Q-ALE are thus instumental for studies of both the etching process and surface damage effects.

For Si etching experiments, we have used a commercial Inductively Coupled Plasma RIE Takachi™ tool from Plasma-Therm LLC, USA. The tool operates in a Cl_2-molecular activation regime using Ar RF-plasma to desorb the etch reaction products in the etch step. Unpatterned silicon-on-insulator (SOI) 10x10 mm^2 samples with a 50 nm thick top Si layer were used for the etching experiments and characterised by spectroscopic ellipsometry and AFM. Typically, the Q-ALE operated in a 25 cycle mode, sufficient to measure the Si thickness difference by ellipsometry using a 4-layer model. A Retarding Field Energy Analyzer (RFEA) from Impedance LLC, Ireland, was installed to measure the Ar^+ ion energy and ion current densities at different Q-ALE conditions, such as RF-power and pressure. The surface effects of the etched SOI samples are characterised by AFM, SEM and Kelvin Probe Force Microscopy (KPFM).

In this work we present the actual data of Ar^+ ion energy distribution and the ion current densities at the sample level in the commercial Takachi™ RIE tool operating in Q-ALE mode. In order to reach a low ion energy regime, we used RF-power in the range of 3-16 W, that corresponds to the bias voltages of 10-120 V. In this voltage range the ion energy peak shifts from ≈50 to 147 eV, respectively, with an increase in the RF-power. The calculated Ar^+ ion flux from the measured ion currents is about $3x10^{13}$ – $2x10^{14}$ ion cm^{-2} s^{-1} that fits well with the published data. Etch per cycle (EPC) was measured in both sputtering (no Cl_2) and ALE-regime at different bias set-points (RF-power). A clear EPC plateau for the ALE regime was observed at biases of 20-40 V that corresponds to the peak Ar^+ ion energy of 50-70 eV. The AFM and high-resolution SEM data demonstrated a decreased surface roughness of etched Si in the plateau region indicating a low surface damage. More details to be presented.

9:15am **ALE1-WeM-6 Atomic Layer Etching Study of Polycrystalline, Epitaxial and Doped ZnO Films Using *in Situ* Spectroscopic Ellipsometry***, **Terrick McNealy-James**, N. Berriel, B. Butkus, T. Currie, T. Jurca, P. Banerjee,* University of Central Florida

Atomic layer etching (ALE) offers sub-nm level control over film removal, with two distinct categories: ion-driven anisotropic etching and thermal isotropic etching. Both options present a promising solution to address patterning challenges in device manufacturing. These mechanisms become particularly important when the extended atomic structure of films such as crystal facets, grain boundaries, and dopants are taken into consideration.

In this work, we study the ALE of a model film - zinc oxide (ZnO), with particular emphasis on observing the role of crystallinity and doping in determining film etch rates. We employ *in situ* spectroscopic ellipsometry as our tool of choice and comprehensively map the etch rate as a function of temperature and co-reactant pulse times. The resulting 3D contour plot of etch rate *vs*. temperature and time depicts the process parameter window. Importantly, the plot is visually appealing and can yield insightful information pertaining to ALE processes, in general.

The ALE chemistry[1] employed to etch ZnO consists of alternate pulses of acetylacetone and O_2 plasma while the temperature is varied from 100 ^oC to 300 ^oC. The etch rates of single crystalline (*e.g.*, c-axis oriented) films are compared with polycrystalline ZnO. The effect of dopants, such as Al^{3+} and Ti^{4+}, on the etch rates of ZnO films are explored. The impact of ALE chemistry in determining etch rates in films with extended atomic structure such as crystal facets, grain boundaries and dopants are discussed with implications to future device manufacturing.

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9:30am **ALE1-WeM-7 Atomic Layer Etching of Diamond for Epitaxy Preparation***, **Julian Michaels,*** University of Illinois at Urbana-Champaign*; N. Delegan,* Argonne National Laboratory, USA*; Y. Tsaturyan,* University of Chicago*; J. Renzas,* Oxford Instruments Plasma Technology*; D. Awschalom,* University of Chicago*; J. Eden,* University of Illinois at Urbana-Champaign, USA*; F. Heremans,* Argonne National Laboratory, USA

Renowned for its exceptional hardness and chemical impermeability, diamond is a wide bandgap semiconductor material with promising applications in optoelectronics, quantum optics, and beyond. Despite its desirable properties, the inherent manufacturing and fabrication challenges associated with monocrystalline diamond make it difficult to smooth, leading to lossy devices in its various applications. Moreover, existing methods for surface smoothing are often costly and time intensive.

In this context, atomic layer etching (ALE) emerges as a potentially viable solution for smoothing diamond surfaces. ALE is a cyclical process that precisely defines nanostructures by removing individual atomic layers. Recently, bias-pulsed ALE (BP-ALE), which is an augmented ALE process wherein reagent gases are not purged between steps, was shown to drastically smooth the surface of 4H-SiC substrates.

Here, we present a novel BP-ALE recipe tailored for diamond substrates. This innovative approach not only achieves precise etching of diamond but also facilitates rapid surface smoothing compared to existing conventional methods. To evaluate the efficacy of BP-ALE, diamond films were grown on etched surfaces, conventionally smoothed substrates, and commercially purchased substrates. Our findings indicate that BP-ALE not only expedites surface smoothing but also yields growth-ready surfaces suitable for subsequent diamond growth.

In summary, our study underscores the potential of BP-ALE as a cost-effective and efficient method for smoothing diamond surfaces, thereby enhancing their suitability for various optoelectronic and quantum optical applications.

Atomic Layer Etching
Room Hall 3F - Session ALE2-WeM
Selectivity, Metrology and Diagnostics in ALE

Moderators: Dr. Adrie Mackus, Eindhoven University, Netherlands, Prof. Gregory N. Parsons, North Carolina State University

10:45am **ALE2-WeM-12 Interest and Potential of Atomic Layer Etching for Selective Deposition***, **Thierry Chevolleau,*** CEA/LETI-University Grenoble Alpes, France*; M. Jaffal,* University Grenoble Alpes, CNRS, LTM, France*; R. Gassilloud,* CEA/LETI-University Grenoble Alpes, France*; N. Possème,* ST Microelectronics, France*; C. Vallée,* University of Albany*; M. Bonvalot,* University Grenoble Alpes, CNRS, LTM, France **INVITED**

Selective deposition processes have attracted increased research interest in recent years due to their ability to precisely deposit thin films on specific substrate areas (for area-selective deposition) or on surfaces with specific orientations (for topographical selective deposition). These processes require a growth kinetic controlled by precursor/surface interactions with an atomic-scale precision, which usually relies on Atomic Layer Deposition (ALD) techniques with or without plasma assistance (PEALD).

Several approaches have been proposed for selective deposition involving surface inhibition treatments with specific chemical agents (such as self-assembled molecules, small molecule inhibitors, plasma treatment) that increase the nucleation delay during subsequent ALD growth. However, the inhibition behavior eventually deteriorates after exposure to a few ALD cycles, necessitating the removal of nuclei formed on non-growth surfaces and the systematic regeneration of the inhibitor.

Another pathway for selective deposition is to combine ALD with Atomic Layer Etching (ALE). ALE involves self-limiting reactions that occur in a cyclic manner and consisting in a surface modification step followed by a removal step of the previously modified layer. Such a process results in the controlled and selective removal of a thin material layer.

In this presentation, we will focus on the interest and capabilities of ALE or quasi-ALE process for selective deposition. Based on several application examples such as liner deposition, we will highlight potential and related issues by coupling ALD and ALE for topographical selective deposition (growth and etch per cycle, selectivity with respect to the underneath layer, cross contamination...). We will also discuss about tools strategy to combine both ALD and ALE processes.

11:15am **ALE2-WeM-14 Insight into SF_6/H_2 Plasma Mixtures to Expand the Capabilities of ALE***, **Guillaume Krieger**, S. Peeters, B. Vonken, N. Chittock, A. Mackus, E. Kessels,* Eindhoven University of Technology, The Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, The Netherlands

The continuous downscaling of nanoelectronics combined with the ever-increasing diversity in materials and 3D geometries calls for highly precise and selective etching processes. Therefore the atomic layer etching (ALE) community must continue to develop a diverse toolbox of processes to enable both anisotropic and isotropic etching of the library of materials required in IC fabrication. Within this toolbox, recent works involving SF_6:H_2 plasma mixtures have demonstrated promising results for the etching of Si- and Ti-based materials[1,2], with improved selectivity. However the etching mechanism is not yet well understood. Notably, the plasma species responsible for the onset of etching at a specific SF_6:H_2 ratio need to be identified.

Here, we present our first results from quadrupole mass spectroscopy (QMS) and optical emission spectroscopy (OES) measurements on SF_6:H_2 plasma mixtures. The plasma power, pressure and SF_6:H_2 ratio have been varied to observe their respective influence on the plasma composition. OES measurements show a high F radical emission intensity for SF_6 rich plasma mixtures. QMS measurements reveal a maximum intensity of the m/z=20 signal, which could be related to the presence of HF, for a ratio of $SF_6/(SF_6+H_2)$ between 0.24 and 0.3. At this same ratio of plasma mixture, the signal of the m/z=34 mass (*i.e* H_2S) drops drastically while the m/z=89 signal (*i.e* SF_3^+ acting as a fingerprint for SF_6) starts to increase. Interestingly,

under the same conditions, this specific range of gas ratios coincides with the etching onset of TaN at $SF_6/(SF_6+H_2)\approx0.25$. Furthermore, when an oxygen gas exposure step is added in the process, the oxidized TaO_xN_y top-layer can be etched at a smaller $SF_6/(SF_6+H_2)$ ratio≈0.2, equivalent to the etching onset of SiO_2. These results show similarities to the selective ALE process reported by Hossain *et al.*[1] between TiN and TiO_2, occurring at a $SF_6/(SF_6+H_2)\approx0.17$, close to the ratio we report for TaN. By identifying the main trends in the plasma species present in the SF_6/H_2 plasma and comparing these observations to the ALE process window, we aim to improve the understanding of the underlying etching mechanisms. A greater knowledge of this process will help to extend this ALE chemistry to a wider range of materials.

References:

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11:30am **ALE2-WeM-15 Retarding-Field Energy Analyzer as a Tool to Find the Process Window for Plasma-Assisted Atomic Layer Etching and Quasi-Atomic Layer Etching**, ***Yoana Ilarionova**, R. Jam, I. Sharma, O. Danielson, S. Ju, A. Muhammad, D. Suyatin, A. Karimi, J. Sundqvist,* AlixLabs AB, Sweden

As the fabrication of chips gets more demanding, atomic layer etching (ALE) provides a controlled way of etching without the surface damage typically associated with reactive-ion etching (RIE). ALE features 2 main steps – surface modification and etch. If inert-ion plasma is chosen to etch, ion energy makes the difference between ALE and physical sputtering. This is why the ion energy distribution function (IEDF) is a very important property when designing plasma-assisted ALE processes.

In this study, we used retarding-field energy analyzer (RFEA) System from Impedans Ltd for IEDF measurements. This enabled us to effectively find and tune the ALE process windows for Si and III-V materials. The experiments were done with Ar plasma in a few standard etch chambers for inductively-coupled plasma reactive ion etching (ICP-RIE) from different vendors. We examined how different process parameters and their interplay influence the IEDF. This is very important for understanding the right combination of process parameters for ALE and the limitations of quasi-ALE processes that can be achieved with this equipment. This also guides in finding the right hardware modifications for improving the ALE processes and their stability in conventional equipment readily available in research labs and semiconductor fabs. This is also valuable for designing dedicated hardware for ALE processes, especially for industry.

Atomic Layer Etching
Room Hall 3F - Session ALE-WeA

Modeling in Atomic Layer Etching

Moderators: Prof. Dr. Steven M. George, University of Colorado at Boulder, Dr. Dmitry Suyatin, AlixLabs A.B.

1:45pm **ALE-WeA-2 Utilizing Thermodynamic Analysis to Screen Material and Precursor Selection for Selective Thermal Atomic Layer Etching**, ***Landon Keller***, North Carolina State University; *M. McBriarty, B. Zope, M. Moinpour, R. Kanjolia,* Merck KGaA, Darmstadt, Germany; *G. Parsons,* North Carolina State University

Advanced patterning of microelectronic devices requires better understanding and control of chemical mechanisms during atomic scale processing for fabrication of advanced architectures. Thermal atomic layer etching (ALE) is a promising approach to achieve controlled etching and chemical selectivity, but it is not yet widely used in semiconductor manufacturing. To advance ALE, new precursor systems must be identified and discovered to create new viable processed for use in backend applications. In this work, we report a methodology for screening material-precursor systems to be used in ALE using tabulated thermodynamic properties of condensed and gaseous compounds.

Previously, our group developed an ALE process for etching TiO_2 ALD films using WF_6/BCl_3.[1] Using our learning from this process, we performed thermodynamic analysis of Gibbs free energy values and equilibrium compositions using a software package called HSC Chemistry 10.[2] The HSC software generates equilibrium composition diagrams and predicts reactions products in a closed system that can be analyzed through an iterative approach to predict process conditions where reactions should occur thermodynamically and identify conditions for ALE or continuous vapor etch (CVE) across a temperature range. Figure 1a shows that after exposure of TiO_2 to WF_6, solid surface products TiF_4(s) and WO_3(s) are predicted to form from 50°C-195°C. TiO_2 was also exposed to BCl_3 and solid B_2O_3(s) is expected to form across the entire temperature range, as shown in Figure 2b. To mimic an ALE process, the solids formed in Figure 1a were exposed individually to BCl_3 and results are shown in Figures 1c-1d. Solid conversion layers generated on the surface after BCl_3 exposure were next exposed to WF_6 to represent a 2nd ALE cycle. Solid products WO_2Cl_2(s) and B_2O_3(s) were predicted to form and the resulting products after exposure to WF_6(g) are shown in Figures 1e-1f. Figures 1a-1b predict CVE of TiO_2 to occur using WF_6 and not BCl_3 over the temperature range 195°C-400°C. When all the equilibrium species are analyzed together, ALE of TiO_2 is predicted to be possible from 155°C-195°C, with no etching occurring below 155°C. This methodology was repeated with 3 other material systems and their predicted CVE and ALE temperature ranges are shown in Table 1. These results can be compared with experimental data to assess the validity of the predicted temperature ranges.

We believe these findings provide a reliable methodology to predict material-precursor systems for CVE and ALE and will aid with the discovery of new etch systems for atomic scale processing within semiconductor manufacturing.

2:00pm **ALE-WeA-3 Atomistic Surface Processing Simulations: ALE of Transition Metal Dichalcogenides**, ***Suresh Kondati Natarajan***, *N. Pandey, J. Schneider, J. Wellendorff,* Synopsys Denmark ApS, Denmark

Atomic Layer Etching (ALE) is becoming a key thin-film processing technique to enable next-generation semiconductor technology nodes. As ALE employs cyclic processing of materials using sequential self-limiting surface reactions, it can be used in conjunction with atomic layer deposition (ALD) to prepare conformal and smooth nanoscale patterns of extreme limits in semiconductor device fabrication. One of the upcoming ALE applications is preparing CMOS channels based on novel transition metal dichalcogenide (TMD) materials, such as MoS_2, WS_2, $MoSe_2$, and others, which may in time replace silicon. TMDs consist of three atomic planes forming a single layer, and the process to etch TMDs must ensure the removal of the three atomic planes conformally to avoid impurities [1]. The layer-by-layer etching process of TMDs therefore needs special considerations to ensure high conformality, avoid over/under etching of TMD layers, and at the same time provide maximum process capability and yield. In the process of adding or removing surface material atom-by-atom, in-silico atomic-scale modeling approaches are key to understanding mechanisms, finding optimal energies of the reacting species for maximum yield, and predicting process outcomes. Synopsys has developed an industry-grade simulation framework within the Synopsys QuantumATK software [2,3] for atomistic surface processing and have previously demonstrated it for ALD of HfO_2 [4].

In this talk, we will present enhancements of this simulation workflow to simulate ALE processing of TMDs (specifically MoS_2), using sequential Cl_2 plasma exposure and Ar ion bombardment [1]. The simulation workflow involves molecular dynamics simulations with specifically trained machine-learned force fields (ML FFs) and can in principle be applicable to ALE processing of any material.

We will first discuss the simulated saturation profiles of Cl uptake during the Cl_2 plasma pulse along with the trend in the dissociative sticking probability/coverage of Cl_2 molecules as a function of its impact energy. Following that, we will showcase the results for the etch rate during cyclic exposure of Cl_2 plasma and Ar ion along with a list of possible etch by-products. Finally, we will discuss the effect of Ar impact energy and impact angle on the etch rate (yield) at saturated Cl coverage.

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2:15pm **ALE-WeA-4 Gas-Phase Etching Mechanism of Amorphous Hydrogenated Silicon Nitride by Hydrogen Fluoride: A Theoretical Study**, ***Khabib Khumaini***, *Y. Kim, R. Hidayat, T. Chowdhury, H. Kim,* Sejong University, Republic of Korea; *B. Cho, S. Park,* Wonik IPS, Republic of Korea; *W. Lee,* Sejong University, Republic of Korea

Understanding the etching reaction mechanism is essential for the design and optimization of the etching process. However, the theoretical study of the etching mechanism is challenging due to the significant influence of crystallinity and impurities. Gas-phase etching of silicon nitride using hydrogen fluoride (HF) vapor provides an alternative to wet etching, particularly for addressing pattern-leaning issues in nanoscale structures. The etching process is continuous at elevated temperatures but exhibits self-limiting behavior at low temperatures [1]. Nevertheless, the atomic-scale mechanism remains poorly understood. Therefore, we performed density functional theory (DFT) calculations to study the etching mechanism [2]. Since silicon nitride films are typically amorphous with significant hydrogen impurities, we created an amorphous substrate model with a hydrogen concentration of 25 at.%. We then constructed four different slab models representing different degrees of fluorination and simulated fluorination pathways. All of the fluorination reactions were exothermic, but the activation energies varied. The cleavage of Si–N or Si–Si bonds and the release of byproducts showed low activation energies, indicating that etching would be plausible. We also simulated the formation and desorption of the $(NH_4)_2SiF_6$ salt on the fluorinated surface. The salt formation was also favorable due to low activation energies, which explains the self-limiting behavior of silicon nitride etching at low temperatures. However, at 152°C or higher, $(NH_4)_2SiF_6$ would decompose into gaseous byproducts, which explains the high etch rate at elevated temperatures. Our DFT calculation using the hydrogenated amorphous silicon nitride slab model successfully explained the etching of silicon nitride films by HF, which a crystalline Si_3N_4 slab model could not explain. Therefore, a slab model with the same composition and structure as the thin film to be etched is required to simulate the etching process.

Acknowledgments This work was supported by the Technology Innovation Program (Public-private joint investment semiconductor R&D program (K-CHIPS) to foster high-quality human resources) (RS-2023-00232258) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (1415187368).

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2:30pm **ALE-WeA-5 Dynamic Global Model of Cl_2/Ar Plasmas for Atomic Layer Etching of GaN**, ***Tojo RASOANARIVO****, C. Mannequin,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean ROUXEL, France*; F. ROQUETA, M. BOUFNICHEL,* STMicroelectronics, France*; A. RHALLABI,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean ROUXEL, France

Plasma Atomic Layer Etching (ALE) is an etching cyclic process. One ideal ALE cycle consists of two self-limited half reactions, separated by purge: an adsorption step to modify the uttermost surface layer and an activation step to selectively remove the modified layer without etching the underneath non-modified layers with an atomic scale resolution. ALE of GaN by alternating Cl_2 and Ar plasma, for the adsorption and activation steps, respectively, has been extensively studied [1]. In these processes, adsorption step is believed to rely on surface modification by chlorine radicals while activation is achieved by selectively controlling the energy of an ionic bombardment. However, these studies mostly focus on experimental approaches and modelling investigations are scarce.

As ALE is atomically sensitive, to better understand plasma/surface interactions at atomic scale, we must first precisely investigate plasma dynamics during the change from Cl_2 to Ar plasma corresponding to the transition from the adsorption to activation step. To date, global models have been well implemented to determine the plasma composition at specific plasma reactor parameters, with good computational time effectiveness [2]. These global models were initially designed to describe plasmas in steady-state conditions [3] and without considering any time dependent variations of the feedgas.

In this work, we develop a dynamic global model for Cl_2/Ar plasmas that follows time evolution of the plasma over a complete ALE cycle by modelling feedgas switches and RF power variations. Our model allows the calculation of neutrals and ions densities evolution over time, especially during the dynamic feedgas switch from a Cl_2 to an Ar plasma. We investigate the effects of the operating conditions such as RF power, pressure and total feedgas flowrate on the evolution of species densities and electron temperature. Higher chlorine species densities can be attained during the Cl_2 to Ar transition compared with a pure Cl_2 plasma. Long residence times for Cl_x species open the question on how to precisely control the surface reactions in GaN ALE.

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2:45pm **ALE-WeA-6 A Transient Surface Site Balance Model for Si-Cl2-Ar Atomic Layer Etching**, ***Joseph Vella,*** Princeton Plasma Physics Laboratory*; D. Graves,* Department of Chemical and Biological Engineering Princeton University and Princeton Plasma Physics Laboratory

Plasma-assisted atomic-layer etching (ALE) processes have the potential to attain controlled substrate removal.[1] While ALE is used in industry, there is still a lack of fundamental understanding surrounding many aspects of the processes. Simulation and modeling can help fill knowledge gaps, which will lead to the development of more efficient ALE processes. Previously, we have focused on modeling Si-Cl2-Ar ALE using molecular dynamics (MD) simulations, which have been validated against experiments.[2-4] We use the results from the MD simulations to develop a transient surface site balance model inspired by the work of Gray et al.[5] and Chang et al.[6] Within the model, the Si substrate is divided into three regions: the top, the mixed, and the crystalline layers. The model considers both the chlorination (surface modification) and ion bombardment (removal) sub-steps. The model accounts for Si and Cl present in the top and mixed layers of the substrate and thus all etched and sputtered products. Mixing of Cl from the top layer into the underlying mixed layer is also modeled. It is shown that this model accurately reproduces MD and select experimental results. The transient site balance model provides an intuitive methodology for modeling ALE processes and can be generalized to more complex processes and materials.

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3:00pm **ALE-WeA-7 Theoretical Analysis on Halogenation of Transition Metal Surfaces toward Thermal Atomic Layer Etching**, ***Hyun Cho****, M. Kim, B. Shong,* Hongik University, Republic of Korea

In fabrication of the semiconductor devices involving three-dimensional structures with shrinking sizes, challenges in etching processes are being emphasized, such as roughness and selectivity issues. Atomic layer etching (ALE) is a possible alternative etching technology that removes small designated amount of material per process step in a self-limiting manner, resulting in precise control over the etch thickness and reduced roughness. Especially, in order to enable isotropic etch processes at the inner surfaces of three-dimensional substrates, thermal ALE processes comprised entirely of reactions of neutral reactant molecules are desirable. Many recent reports on thermal ALE utilize halogenation reaction at either conversion or volatilization steps. Since such surface reactions strongly depend on the substrate materials and halogenation reactants, it is desirable to identify the reactivity of possible self-limiting halogenation according to the reactant-substrate combinations. In this study, we conducted an analysis on the energetics of the surface halogenation of some transition metal surfaces, using density functional theory (DFT) and machine learning potential (MLP) calculations. By calculating the adsorption energy of Cl and F atoms depending on their surface coverage, as well as the energy change in conversion into metal halide overlayers, the spontaneity according to the degree of halogenation could be compared. The different reactivities of several molecular chlorination and fluorination agents, such as Cl_2, F_2, $SOCl_2$, and SF_4, are also compared.

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