Sunday Evening, July 23, 2023

Atomic Layer Etching
Room Evergreen Ballroom & Foyer - Session ALE-SuP
Atomic Layer Etching Poster Session

ALE-SuP-1 Chemical Approaches to Atomically Controlled Etching of Tertiary Materials and van der Waals Solids*, **Marissa Pina**, M. Whalen, J. Xiao, A. Teplyakov,* University of Delaware

$CrPS_4$ is a 2D van der Waals material with layer-dependent ferromagnetic behavior. While monolayer $CrPS_4$ has a ferromagnetic out-of-plane spin orientation, alternating antiferromagnetic/ferromagnetic behavior was demonstrated for an even vs. odd number of layers. This interesting set of properties makes the material a potentially outstanding candidate for spintronic devices; however, obtaining a specific number of layers on any support surface is currently impossible. Mechanical exfoliation methods can reduce the number of layers to a certain extent, but more controlled methods will be needed to further reduce the thickness of the crystal to the monolayer thickness. Thus, atomically precise methods of etching would be extremely desirable for $CrPS_4$.

The problem with designing atomic layer etching (ALE) approaches for materials containing two or more elements is that the overall chemistry should be equally efficient in removing all the elements simultaneously. We have previously demonstrated that a very efficient method can be applied to etch a tertiary material CoFeB alloy with atomic precision, and it would be expected that for a layered material, such as $CrPS_4$, the van der Waals nature of interlayer interaction would make it easier to design a chemical method to remove the material layer-by-layer. In this work, $CrPS_4$ flakes were exfoliated onto a SiO_2 substrate from a single crystal. Atomic force microscopy was used to determine that the deposited flakes were up to 100 nm thick and several microns wide, with a wide size distribution of shapes and thicknesses. We first used XPS to evaluate the susceptibility of this material to oxidation and then, using an ultra-high vacuum chamber, we heated the sample and exposed it to a specific exposure of acetylacetone in what we define as a cycle. Repeating atomic force microscopy on the flakes, we found an average etch rate of 1.6 nm/cycle. Although the exact etching conditions have to be optimized and chemistry of the etching process has to be determined, these initial experiments promise a successful method for ALE of this material that can also possibly be applied to other van der Waals crystals.

ALE-SuP-2 Electron-Assisted Silicon Etching in an Inductively Coupled CF_4 Plasma via Low-Energy Electron Beam*, **Jiwon Jung**, C. Lim, C. Chung,* Hanyang University, Republic of Korea

Low-energy electron-assisted silicon etching is conducted using an inductively coupled CF4 plasma at a pressure of 4 mTorr. During silicon etching, a low-energy electron beam is generated and controlled by varying the electron acceleration voltage (0-60 V) on grid to assist silicon etching. Silicon etch rate is increased with increasing acceleration voltage, this is because electron beam energy is also increased. By using low-energy electron beam, low-damage etching can be achieved because mass of electron is smaller than that of ion. To observe the damage variation of silicon before and after the low-energy electron-assisted etching process, XPS measurement is conducted.

ALE-SuP-3 Damage-Free Graphene Etching by Ultra-Low Electron Temperature Plasma*, **Junyoung Park**, J. Jung, M. Kim, C. Lim, B. Seo, C. Chung,* Hanyang University, Korea

The effect of ultra-low electron temperature(ULET, $T_e < 0.2$ eV) on multi-layer graphene etching is investigated. During the etching process using plasma, problems such as substrate damage due to high ion bombardment energy occur, which have a fatal effect on process yield and reliability. In particular, high-strength and high-performance semiconductors are required in recent years, achieving precise etching without damage at the atomic scale is essential. To solve this problem, ULET plasma is generated whose electron temperature is about 20 times lower than that of the conventional inductively coupled plasma(ICP) ($T_e \sim 4$ eV), and damage-free etching using the ULET plasma is studied. Plasma-induced damage on the wafer is mainly caused by ion bombardment, and the ion bombardment energy is proportional to the sheath voltage. Since the sheath voltage is proportional to the electron temperature, the ion bombardment energy can be minimized by generating ULET plasma. To confirm the damage-free etching effect of ULET plasma, multi-layer graphene is exposed to conventional ICP and ULET plasma, respectively. In the case of graphene exposed to conventional ICP, the crystal structure of graphene is damaged by plasma. On the other hand, when exposed to ULET plasma at the same electron density and time as the conventional ICP, damage does not occur. This confirms that plasma damage due to ion bombardment may be removed using ULET plasma. The removal of the graphene layer was verified by Raman spectroscopy, and T_e was obtained by measuring the electron energy probability function (EEPF).

ALE-SuP-4 Anisotropic Atomic Layer Etching of Molybdenum by Formation of Chloride/Oxychloride*, **Yun Jong Jang**, D. Kim, H. Kwon, H. Gil, G. Kim, D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

As the degree of integration of semiconductor devices increases, the line width between patterns of interconnects continues to decrease. In order to solve this challenge, Cu having low resistivity is currently used as an interconnect material with a barrier material in a damascene structure. But, Cu shows a rapid increase of resistivity in a critical dimension (CD) of less than 10 nm due to long mean free path in addition to a limitation in scaling down due to the requirement of a barrier material. Therefore, need for a new material such as Mo, Co, Ru, etc. to replace Cu has been increased to solve this problem. In this study, atomic layer etching (ALE) of Mo has been carried out by using O_2 and Cl_2 as adsorption gases and Ar^+ ion beam for desorption. By using inductively coupled plasma (ICP)-type ion beam for desorption step, it was possible to precisely control the ion energy during ALE. In the adsorption step, the surface of Mo was modified into $MoCl_x$ and MoO_xCl_y using O_2 and Cl_2. In the desorption step, the modified Mo surface was removed using an Ar^+ ion beam. After the process, physical and chemical damage on the surface was analyzed using X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), etc.

ALE-SuP-5 New Oxidants for Cu ALE*, **Persi Panariti**, A. Hock,* Illinois Institute of Technology

Atomic Layer Etching of copper is an important challenge when it comes to scaling down electronic devices to sub-10 nm dimensions. ALE of copper is of considerable interest, because copper is widely used an interconnect material for integrated circuits, due to its excellent electrical conductivity, good electromigration resistance and low cost.

ALE of metallic surfaces typically proceeds in two steps, the first being surface activation, followed by the introduction of an organic ligand to yield a volatile metal complex. ---The activation step (oxidation) is especially important for enabling ALE, because metallic Cu surfaces are chemically inert. Another important factor is the ability to control the oxidation *strength* and *reactiondepth* of the oxidizing agent. Several oxidants for metallic Cu surfaces have been reported in the literature, such as ozone, hydrogen peroxide, oxygen plasma etc. These oxidants are aggressive and have numerous issues, such as oxidizing up to several nm of Cu and increasing surface roughness, especially at elevated temperatures. These are undesirable outcomes for ALE, because the oxidized copper surface should remain as uniform as possible after oxidation, so that the etch step yields a smooth and conformal Cu surface. Thickness of greater than a few nm can be incompatible with scaling. Therefore, there is a need for more tunable oxidants, that allow for better control of the oxidation strength and depth of Cu thin films. We have investigated several oxygen atom transfer reagents that formally transfer an oxygen atom to a Cu surface. The oxidation strength of these reagents was probed by *in-situ* X-Ray Absorption Spectroscopy (XAS) on Cu nanoparticles, as well as in real ALE conditions, where the ALE reactions were studied by *in-situ* QCM.

ALE-SuP-6 Atomic Layer Etch Development of Noble Metals Cu and Pt for Mram Technologies*, **Omar Melton**, R. Opila,* University of Delaware

Magnetoresistive random-access-memory (MRAM) is a leading option for non-volatile digital data storage. Due to the combination of the broad range of materials in the device, improving the fabrication methods is challenging. Currently, MRAM technologies mainly rely on epitaxial, atomic layer deposition (ALD), methods to generate the thin layers necessary for ideal performance. Atomic layer etching (ALE), as a time reversed ALD method, has potential for accurately etching nearly all materials, particularly those that cannot be deposited with precision. Herein, we propose the etching of noble transition metals, copper (Cu) and platinum (Pt), and etch stop testing of the tunneling barrier (MgO). The etch is conducted using a thermal approach, rather than commonly used plasma methods, where the film is etched by sequential dosing with to two different chemical moieties, chlorine and acetylacetone (acac). Thus, permitting kinetic factors to overcome thermodynamic limitations, thereby developing a controlled etch driving towards one atomic layer at a time. Results demonstrate that Cu is etched under comparatively mild conditions, whereas Pt requires more aggressive temperatures and pressures to facilitate the etch.Furthermore, MgO exhibited resistance to etching upon exposure to these conditions.

ALE-SuP-7 Layer-by-Layer Etching of 2D Palladium Diselenide, ***Ji Eun Kang***, *Y. Ji, S. Choi, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Recently, there has been a widespread interest in developing high-performance broad band photodetector of 2D materials for sensing, imaging, and spectroscopy. Among them, Palladium diselenide ($PdSe_2$) has emerged as a promising candidate for the future device application due to its large tunable band gap (from 0 eV to 1.3 eV), high electron mobility, and outstanding environmental stability. To obtain mono to multi-layer of $PdSe_2$, various methods such as exfoliation, chemical vapor deposition, and etching can be used. However, in the case of exfoliating or deposition, it is difficult to precisely control the layer, and, in the case of reactive ion etching, it may cause unwanted structural damage in $PdSe_2$ because $PdSe_2$ has a “puckered” structure. In addition, its interlayer coupling is strong, so it can be easily transformed from $PdSe_2$ semiconducting phase to $PdSe_{2-x}$ metallic phase by ion irradiation. In this study, $PdSe_2$ was removed layer-by-layer without damage by applying cyclic isotropic etching through oxidation and organic vapor treatment. And it was confirmed that the etching was performed precisely one layer per one cycle without damaging the $PdSe_2$ puckered structure.

ALE-SuP-8 Cyclic Dry Etch Process of SiO_2 using H/F radicals and Methanol Vapor, ***HaeIn Kwon***, *H. Gil, D. Kim, Y. Jang, D. Kim, G. Kim, D. Kim, G. Yeom,* Sungkyunkwan University, Republic of Korea

In the cleaning of deep contact holes, wet etching process is generally used, but there are issues such as inability to etch the bottom of the deep contact holes in nano-size patterns. Therefore, new dry cleaning process is necessary to replace the existing wet etching process for next-generation semiconductor devices. Previously, as dry cleaning processes (or as isotropic etching processes) of SiO_2 for deep contact holes, HF/NH_3 vapor process or the NF_3/NH_3 plasma process has been investigated. However, ammonium salt formed in the process using NH_3 can form solid powders and it may form particles in the process chamber. Therefore, in this study, H/F radicals and Methanol vapor were used for the isotropic cyclic etching of SiO_2 to obtain high selectivity of SiO_2 over Si_3N_4 and Si. HF was formed using a NF_3/H_2 remote plasma and, to remove the F radicals, methanol vapors were injected using shower ring located at the outside the plasma discharge region. Under the optimized conditions, the etching depth per cycle of SiO_2 was about ~13 nm/cycle and the selectivity with Si_3N_4 and Si were over 50 and 20 respectively. Surface chemistry and roughness were investigated at each process step using XPS (X-ray photoelectron spectroscopy), FT-IR (Fourier-Transform Infrared Spectroscopy), and AFM (Atomic Force Microscope).

ALE-SuP-9 Quantum Chemistry Modeling of Plasmaless Anisotropic Etching of Silicon by F2 Molecule, ***Yuri Barsukov***, *O. Dwivedi, S. Jubin, I. Kaganovich,* Princeton University Plasma Physics Lab

Anisotropic etching is often used in the semiconductor industry. One of the possible applications is silicon nano-scale texturing for black silicon production. Plasmaless etching can be used for surface texturing if the etch rate depends on the crystal surface orientation and, as a result, the surface is removed faster in one crystal surface direction compared to another. It was experimentally observed that F2 molecules preferentially etch silicon on (100) and (110) faces but very little on (111) at room temperature. We performed quantum chemistry modeling of this process by studying the reaction of F2 dissociative adsorption on fluorinated Si(100), Si(110), and Si(111) surfaces. The reaction probabilities were calculated using DFT (density functional theory) in combination with transition state theory. We established that the energy barrier of F2 dissociation on the Si(111) surface is significantly higher than on Si(100) and Si(110). The reason for high reactivity on Si(100) and Si(110) is that all Si atoms on fluorinated (100) and (110) oriented surfaces are bonded with fluorine atoms. The passivating F atoms attract electrons from Si atoms and, as a result, all Si atoms are positively charged. At the same time, half of the atoms on the fluorinated Si(111) surface are negatively charged, because they have no bonds with the fluorine atoms. The negatively-charged Si atoms on Si(111) create an additional repulsive force with the partly negatively-charged F2 molecule during the dissociation and increase the reaction barrier. Assuming that F2 dissociation is the rate-determining step of the etching process, we compared the calculated rate of F2 dissociation on Si(100) and measured the etch rate of Si(100) by F2. The calculated rate of dissociation matches experimental etch rate well.

ALE-SuP-10 Atomic Layer Etching of Mo with Surface Fluorination and Ion Bombardment, ***Yongjae Kim***, *H. Kang, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Resistance of Cu significantly increases in the line width of interconnect below 10 nm due to the electron scattering in the grain boundary and side wall, and the resistance can be reduced by replacing Cu with alternative metals such as Co, Mo, and Ru, which have lower electron mean free path compared to the Cu. [1, 2] Among them, Mo is strong against the electromigration than the Co and Ru due to the highest melting point and cohesive energy. Interconnect metal line based on Mo can be fabricated with reactive ion etching (RIE) due to low boiling point of molybdenum fluoride and ruthenium fluoride compared to the copper fluoride. However, RIE is facing challenges in making nanometer scale patterns in terms of precise etch rate control and surface roughness. Atomic layer etching (ALE) can remove layers with atomic scale precision, low surface roughness, and excellent uniformity compared to the RIE.

In this work, ALE process was developed for Mo in an inductively coupled plasma (ICP) reactor. The Mo surface was fluorinated with C_4F_8 or CHF_3 plasmas, and fluorinated surface was etched by ion bombardment using Ar plasma. The C_4F_8 plasma generates fluorine-rich fluorocarbon layer on the Mo surface compared to the CHF_3 plasma. Etch per cycle (EPC) of Mo was investigated with dependence of ion energy and etching time. ALE window, or constant EPC was observed in the energy range of 100 ~ 225 V for Mo. The EPC of Mo was determined to be 2.8 nm/cycle for C_4F_8 plasma and 0.8 nm/cycle for CHF_3 plasma in the ALE window region. Etch residues and surface roughness were compared with radical etching, RIE, and ALE. Lowest etch residues and surface roughness were confirmed with ALE process compared to the radical etching and RIE.

References

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Keywords: Plasma atomic layer etching, Molybdenum, ALE window, Etch residues, Surface roughness

ALE-SuP-11 Thermal Atomic Layer Etching of Palladium with Chlorination and Ligand Volatilization, ***Hojin Kang***, School of Chemical Engineering, Sungkyunkwan University (SKKU), Korea (Democratic People's Republic of)*; Y. Kim,* SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Korea (Democratic People's Republic of)*; A. Cho,* Department of Chemical and Biomolecular Engineering Korea Advanced Institute of Science and Technology (KAIST), Korea (Democratic People's Republic of)*; H. Jung,* Department of Chemical and Biomolecular Engineering Korea Advanced Institute of Science and Technology (KAIST) Daejeon, 34141, Republic of Korea3, Korea (Democratic People's Republic of)*; S. Cho, H. Chae,* School of Chemical Engineering, Sungkyunkwan University (SKKU), Korea (Democratic People's Republic of)

Palladium (Pd) hydrogen sensors operate by the change in electrical resistance according to volume expansion [1]. Thinner Pd leads to shorter paths for hydrogen gas molecules, resulting in lower hydrogen concentration and increased sensitivity of the sensor for volume expansion. Conventional wet and dry etch processes face challenges in achieving precise thickness control and uniformity [2]. Atomic layer etching (ALE) processes can remove sub-nanometer layers with precision [3]. In this work, thermal ALE process for Pd was developed with surface chlorination with Cl_2 plasma and ligand volatilization with NH_3 gas in a capacitively coupled plasma (CCP) reactor. In the chlorination step, the Pd surface was converted into $PdCl_2$. The thickness of $PdCl_2$ was increased from 1.0 nm to 2.9 nm as the process temperature increased from 25 to 300 °C, and that of $PdCl_2$ was saturated to 1.6 nm after 30 seconds of Cl_2 plasma time at a process temperature of 150 °C. In the ligand volatilization step, the $PdCl_2$ layer was removed with ligand volatilization using NH_3 gas at the temperatures above 150 °C. The etch per cycle (EPC) of Pd was in the range of 0.8~1.6 nm/cycle with increasing NH_3 gas injection time, and the EPC was saturated to 1.6nm after 30 seconds of NH_3 injection time. The surface roughness increased from 0.3 nm to 0.4 nm after 20 ALE cycle.

ALE-SuP-12 Plasma Enhanced Atomic Layer Etching of Zirconium Oxide using Plasma Fluorination and Ligand Exchange with $TiCl_4$, ***Hyeongwu Lee***, *Y. Kim, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Dynamic random access memory (DRAM) capacitor consists of electrodes and dielectric materials, and the dielectric thickness has been continuously reduced to increase capacitance. However, reducing the dielectric dielectric thickness also increases the leakage current. The leakage current can be decreased by applying thin crystalline ZrO_2 film, which has a high dielectric constant of 39. A thin crystalline ZrO_2 film can be produced by depositing a thick crystalline film and then using atomic layer etching (ALE) to reduce the film thickness. Thermal ALE can precisely control the etch depth at the atomic scale and remove materials in every direction. In this work, a thermal ALE process was developed for ZrO_2 with two steps of plasma fluorination and ligand-exchange with titanium chloride($TiCl_4$). In the fluorination step, ZrO_2 surface was fluorinated with fluorine-containing plasmas to form zirconium oxyfluoride. The formation of Zr-O-F bond was confirmed by X-ray photoelectron spectroscopy analysis. In the ligand exchange step, the fluorinated layer was removed with $TiCl_4$. The etch per cycle of ZrO_2 is saturated at 1.3 Å/cycle after 60 seconds of $TiCl_4$ exposure time. Post plasma treatment was developed to remove fluorocarbon residues on the surface with O_2 and NH_3 plasmas after ALE process. The root mean square (RMS) roughness of ZrO_2 decreased from 0.81 nm after 30cycles of ALE to 0.64 nm after post plasma treatment.

Atomic Layer Etching
Room Grand Ballroom H-K - Session ALE-MoA

Metal ALE

Moderators: Dr. Thorsten Lill, Lam Research Corporation, Dr. Tristan Tronic, Intel Corporation

4:00pm **ALE-MoA-11 Wet Atomic Layer Etching of Metals***, **Paul Abel**,* Tokyo Electron America, Inc. **INVITED**

Here we present a new strategy for implementing atomic layer etching (ALE) of metals using wet chemistry at room temperature. Unlike plasma- and thermal-ALE, material removal in wet ALE is achieved through dissolution of the self-limiting passivation layer rather than volatilization. This relaxes the temperature requirements of thermal ALE, and the sputter threshold requirements for plasma ALE. Solubility is strongly dependent on solvent species, so solvent exchange can be used as the trigger for release of the self-limiting passivation layer as an alternative to ligand exchange. In the first half of the etch cycle, a self-limiting metal-ligand surface complex is formed on exposure to the first etch solution. The surface layer must be insoluble in this solution, but readily soluble in the second etch solution in order to complete the ALE cycle. Additionally, the second solution must be unreactive with the freshly exposed metal surface. Sequential exposure to both etchants is required for material removal. A diagram of this wet ALE process is shown in Figure 1.

Most transition metal complexes form around oxidized metal centers, so formation of the surface complex is governed by solution redox chemistry in the presence of appropriate ligands. Solubilization of this complex can be achieved in one of several ways. Solvent exchange can be used to dissolve the layer in an appropriate solvent. Ligand exchange in a non-redox active solution can be used to alter the solubility of the surface complex without changing the solvent or reacting with the underlying substrate. And lastly, ion exchange can be used if the surface complex is a coordination compound containing both a ligand-bound complex ion and a counterion.

In this talk, we apply these strategies to the wet ALE of copper and cobalt. These metals easily form thick native oxide layers. The thickness of this layer, as well as the ease with which it forms makes it inappropriate to use as the modified layer for wet ALE. Exposure to an appropriate ligand-containing solution, however, forms a monolayer of metal-ligand complex on the native oxide surface. This metal-ligand complex is a much more appropriate modified layer, and the etch amount per cycle is strongly dependent on ligand chemistry. Both ligand surface packing density and ligand binding strength influence the metal removal rate. Selective removal can then be accomplished through either a solvent exchange to directly dissolve the modified layer or a ligand exchange to form a more soluble compound through reactive dissolution.

4:30pm **ALE-MoA-13 Thermal Atomic Layer Etching of Molybdenum Based on Sequential Oxidation and Chlorination Reactions***, **Taewook Nam**, J. Partridge, S. George,* University of Colorado at Boulder

Previous pathways for thermal ALE of metals, such as Cu and Co, have employed either oxidation or chlorination reactions for surface modification followed by either ligand-substitution or ligand-addition reactions for volatile release. This study introduces another mechanism for the thermal ALE of metals using sequential oxidation and chlorination reactions. This mechanism relies on the metal having volatile oxychloride complexes. The thermal ALE of Mo was studied using quartz crystal microbalance (QCM), x-ray reflectivity (XRR), and quadrupole mass spectrometry (QMS) measurements. Mo films were first deposited on quartz crystals or silicon coupons using sputtering. The mass or thickness changes were then measured versus sequential oxidation and chlorination reactions using O_3/O_2 and $SOCl_2$ as the reactants.

The QCM measurements observed very digital mass changes during the sequential O_3/O_2 and $SOCl_2$ exposures. QCM results showed pronounced mass gains during O_3/O_2 exposures and distinct mass losses during $SOCl_2$ exposures. QCM measurements for three cycles of Mo ALE at 175°C are displayed in Figure 1. The mass changes were also self-limiting versus O_3/O_2 and $SOCl_2$ reactant exposure. The mass loss per Mo ALE cycle was -1,600 ng/cm^2 or 15.7 Å/cycle under the saturation reaction conditions at 175°C. The Mo ALE etch rate was studied from 100°C to 250°C and larger etch rates were observed at higher temperatures.

Mo ALE is dependent on the release of volatile oxychloride etch products. For under-saturation reaction conditions, the mass changes during the O_3/O_2 exposures could either be negative or positive. Lower O_3/O_2 exposures led to negative mass changes and higher O_3/O_2 exposures led to positive mass changes. This behavior can be explained based on the volatile oxychloride etch product during Mo thermal ALE. There is chlorine on the surface after the $SOCl_2$ exposure. Initial O_3/O_2 exposures remove the chlorine as a volatile Mo oxychloride product and produce a mass loss. As the chlorine is removed, larger O_3/O_2 exposures can then proceed to oxidize the Mo surface and produce a mass gain.

QMS experiments were performed to identify the etch products. To improve the detection sensitivity, these experiments utilized various powder samples to model the Mo surface after the O_3/O_2 or $SOCl_2$ exposures. The main Mo oxychloride species detected was MoO_2Cl_2. Figure 2 shows the observation of MoO_2Cl_2 during $SOCl_2$ exposure on MoO_3 after a previous O_3/O_2 exposure. The parent $MoO_2Cl_2^+$ ion intensities are observed in a cluster of peaks around m/z 200. All of the main ion intensities are explained by the natural isotopic abundances of Mo and Cl in MoO_2Cl_2.

4:45pm **ALE-MoA-14 Non-Halogen Plasma for Selective Removal of Titanium Compounds Applied in Advanced Atomic Layer Etching***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; K. Shinoda,* Hitachi, Ltd., Japan*; S. Hsiao,* Nagoya University, Japan*; H. Hamamura,* Hitachi, Ltd., Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective removal of metal gate materials such as TiC, TiAlC, TiN, or TiAl is required in the fabrication of next generation field effect transistor (FET) of logic semiconductor devices. In our development of advanced etching methods, we have proposed wet-dry etching or wet-like plasma etching that combines the advantages of wet etching (high isotropy and selectivity) and dry etching (high controllability). For atomic layer etching (ALE) processes, surface modification reduces surface energy of sample surface in the first step, and the modified layer is removed in the next step.

Surface modification of metal carbide TiAlC using floating wire-assisted non-halogen vapor plasma, that can generate a high-density plasma at medium pressure, has been demonstrated in our recent study, indicating a potential of isotropic and selective etching of TiAlC by using chemistries containing NH, H, and OH. In this study, the N-H-O containing plasmas can selectively remove TiAlC over TiN. Film thickness change of titanium compounds was measured by an *in situ* ellipsometer, and surface chemical bonding during the processing was analyzed by an *in situ* attenuated total reflectance-Fourier transform infrared spectrometer. Optical emission spectra of NH and OH molecular lines from plasmas were detected by a high-resolution optical emission spectrometer. The sample surface was analyzed before and after the plasma treatment by X-ray photoelectron spectroscopy.

By controlling the surface reactions, selective removal of TiAlC over TiN can be achieved by its reaction with N-H-O plasma to form volatile products, as firstly proposed here. We emphasized that this non-halogen etching method can be applied for highly selective etching of metal carbide, nitride, or oxide.

5:00pm **ALE-MoA-15 Leveraging Surface Nitridation to Enable Plasma-Thermal Atomic Layer Etching of Ni Based Metals***, **Taylor Smith**, J. Chang,* University of California, Los Angeles

Metals are of increasing importance in modern electronics. For example, Ni and Ni-based alloys have been used for extreme ultraviolet lithography (EUVL) absorber layers and as components in composite multiferroics for magnetoelectric devices. In this work, we present an atomic layer etching (ALE) technique to etch Ni that relies on plasma nitridation to modify the Ni surface and organic vapor exposure to remove the modified layer. Theoretical study by density functional theory has shown that ALE of metals including Ni is possible through nitridation and formic acid (FA) exposure, through the formation of dimeric $Ni_2(HCOO)_4$ and NH_3 as reaction products.[1] Since surface nitridation is not a spontaneous reaction like oxidation upon exposure to ambient air (e.g., moisture), this process can be analyzed more definitively without the convolution of native oxide formation.[2] In this work, we experimentally examined this new method using a remote nitrogen plasma and a custom vapor chamber to modify and etch nickel and nickel based alloys.

A pure nitrogen plasma in a custom planar geometry ICP reactor was used to form the nickel nitride.The thickness of the nitridized layer is controlled by modifying the power, pressure, and exposure time of the plasma and quantified by a combination of spectroscopic ellipsometry (SE) and scanning electron microscopy (SEM).To alleviate the complication in SE analysis by the fact that the optical constants of thin metal films can vary depending on deposition method and thickness, SE measurements of samples that have undergone similar numbers of ALE cycles are fit simultaneously assuming that the optical constants over a narrow thickness range are the same. This improves the thickness measurement accuracy, as corroborated by SEM analysis. FA in the solution phase and vapor phase are both examined as a means of removing the nitridized Ni layer, with X-ray photoelectron spectroscopy (XPS) showing both phases completely removing the N 1s peak that forms after plasma nitridation. The etch rate of Ni by nitridation and FA solution is 6.1 nm/cycle.For the case of a Ni ALE cycle involving plasma nitridation and FA vapor exposure at 80°C, the etch rate was about 1 nm/cycle, indicating a relatively controllable process. For the Ni_xAl_y alloy, both solution phase and vapor phase FA at 80°C removed the nitridized surface layer. However, this led to Al surface enrichment, suggesting the ALE cycle preferentially etched Ni over Al. The selectivity to common hardmasks was also tested.

References

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5:15pm **ALE-MoA-16 Plasma Atomic Layer Etching of Ruthenium with Surface Fluorination and Ion Bombardment for Next-generation Interconnect Metal***, **Yongjae Kim**, H. Kang, M. Choi, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Cu is widely used for interconnect metal in semiconductor devices, but the resistance of Cu increases significantly as the interconnect width decreases below 10 nm due to electron scattering at grain boundary and surface. Ruthenium is one of the candidate materials to replace Cu as the interconnect metal because resistivity of Ru is lower than that of Cu when the interconnect width is less than 10 nm. [1] Reactive ion etching (RIE) is used for direct patterning of metals, but controlling atomic-level film thickness in nanopatterning processes is challenging. Atomic layer etching (ALE) is suggested as an alternative to RIE because ALE can remove layers with atomic scale precision, excellent uniformity, and low surface roughness. [2]

In this work, plasma ALE process was performed for Ru in an inductively coupled plasma (ICP) reactor. The ALE process consists of two steps: surface fluorination with CHF_3, C_4F_8 or CF_4 plasmas and ion bombardment with Ar plasma. The CHF_3 and C_4F_8 plasmas generate fluorocarbon layer on the Ru surface and the CF_4 plasma converts the Ru surface to RuF_x. The C_4F_8 plasma produces fluorine-rich fluorocarbon layer on the Ru surface compared to the CHF_3 plasma. Etch per cycle (EPC) of Ru was investigated according to ion energy and etching time. ALE window of Ru was observed in the ion energy range of 150 ~ 200 V for CHF_3 and C_4F_8 plasmas and 100 ~ 200 V for CF_4 plasma. The EPC of Ru was determined to be 0.6 nm/cycle for CHF_3 plasma, 1.5 nm/cycle for C_4F_8 plasma, and 0.3 nm/cycle for CF_4 plasma in the ALE window region. Chemical sputtering threshold energy of Ru was determined to be 100 V for CHF_3 plasma, 50 V for C_4F_8 and CF_4 plasmas. The EPC of Ru was increased with increasing Ar plasma time and exhibits self-limiting properties at 180 seconds for CHF_3 plasma and at 300 seconds for C_4F_8 and CF_4 plasmas. Surface roughness and etch residues of Ru were compared with RIE and ALE.

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Keywords: Atomic layer etching, Ruthenium etching, Fluorine-contained plasma, Surface roughness, Etch residues

5:30pm **ALE-MoA-17 Comparison of Ruthenium ALE based on ICP and Ion Beam***, D. Kim, H. Kwon, Y. Jang, H. Gil, D. Kim, G. Kim, **Geun Young Yeom**,* Sungkyunkwan University, Republic of Korea

In this study, using etching tools based on both ICP system and ICP-ion beam system, Ru ALEs have been carried out and their etch characteristics were compared. For Ru ALE based on ICP system, RuO_x was formed on the surface using direct O_2 plasma in the ICP system and then RuO_x was removed from the surface using Ar plasma by biasing the substrate. For Ru ALE based on ICP-ion beam system, and where, plasma source and the substrate were separated by grids on the ICP-ion beam source, only O radicals were supplied to the Ru surface using remote plasma to form RuO_x, and then RuO_x was removed using an Ar^+ ion beam. Using both Ru ALE techniques, surface oxidation characteristics according to direct plasma and remote plasma were compared, and desorption methods for realizing ideal atomic layer etching were investigated. In addition, physical and chemical changes occurring on the Ru surface during adsorption and desorption steps were evaluated, and the etching mechanisms were compared.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE-TuM

Modeling of ALE

Moderators: Prof. Dr. Michael Nolan, University College Cork, Dr. Thomas Tillocher, GREMI CNRS/Orleans University

11:15am **ALE-TuM-14 Plasma Oxidation of Copper: Molecular Dynamics Study with Neural Network Potentials***, **Yantao Xia,*** University of California at Los Angeles*; S. Philippe,* University of California, Los Angeles

The formation of thin oxide films is of significant scientific and practical interest. In particular, the semiconductor industry is interested in developing a plasma atomic layer etching process to pattern copper, replacing the dual Damascene process. Using a nonthermal oxygen plasma to convert the metallic copper into copper oxide, followed by a formic acid organometallic reaction to etch the copper oxide, this process has shown great promise. However, the current process is not optimal because the plasma oxidation step is not self-limiting, hampering the degree of thickness control. In the present study, a neural network potential for the binary interaction between copper and oxygen is developed and validated against first principles calculations. This potential covers the entire range of potential energy surfaces of metallic copper, copper oxides, atomic oxygen, and molecular oxygen. The usable kinetic energy ranges from 0 - 20 eV. Using this potential, the plasma oxidation of copper surfaces was studied with large-scale molecular dynamics at atomic resolution, with an accuracy approaching that of the first principle calculations. An amorphous layer of CuO is formed on Cu, with thicknesses reaching 2.5 nm. Plasma is found to create an intense local heating effect that rapidly dissipates across the thickness of the film. The range of this heating effect depends on the kinetic energy of the ions. A higher ion energy leads to a longer range, which sustains faster-than-thermal rates for longer periods of time for the oxide growth. Beyond the range of this agitation, the growth is expected to be limited to the thermally activated rate. High-frequency, repeated ion impacts result in a microannealing effect that leads to a quasicrystalline oxide beneath the amorphized layer. The crystalline layer slows down oxide growth. Growth rate is fitted to the temperature gradient due to ion-induced thermal agitations, to obtain an apparent activation energy of 1.0 eV. A strategy of lowering the substrate temperature and increasing plasma power is proposed as being favorable for more self-limited oxidation.

11:30am **ALE-TuM-15 Multi-scale Simulation Study for the Role of High C/F ratio Plasma on Etch Selectivity of SiO_2 and Si_3N_4 in q-ALE***, **Hojin Kim,** D. Zhang, T. Hisamatsu, A. Ko,* TEL Technology Center, America, LLC, USA

Using multi-scale simulation techniques, we studied how C/F ratio in plasma affected the etch selectivity between Si_3N_4 and SiO_2 with a formed thin FC film on each surface during a q-ALE process. In SAC etching for via or contact holes into oxide to make a contact, nitride also can be etched, resulting in the yield issue. Thus, we need to reduce the nitride loss effectively. However, as the device becomes smaller, it is hard to control to obtain enough selectivity.Previous experiments with various C_xF_y gases showed the enhancement of etch selectivity between Si_3N_4 and SiO_2 with high x/y ratio gas. However, the understanding of the underlying behavior has been not clear. First, we revealed the relationship between intrinsic C/F ratio neutral and species fluxes by using the plasma simulation, observing that high C/F ratio gas could create high C/F ratio radicals. With atomistic Molecular Dynamics (MD) simulation and DFT calculation, we also studied the possible role of C/F ratio on FC film formation on both substrates and following an ion bombardment. MD simulation results showed that with higher C/F ratio plasma, harder and denser FC film could be formed on Si_3N_4 by significantly increasing absorbed carbon (C), Si-C, and C-C bonds. In the SiO_2 case, we could observe many O-C bonds that cause to weaken the formed FC film by converting it to highly volatile materials (i.e., CO_2). The highest C/F ratio gas case showed that significant O-C bonds on SiO_2 were generated. Following the ion bombardment step with both modified substrates, we observed that the highest C/F ratio case exhibited less loss of total atoms and regenerated Si-C bonds, probably a dangling bond behavior. In Si_3N_4, N-C bonds were generated more to protect the substrate but not in SiO_2; O-C bonds were lost during the ion bombardment. We confirmed the surface reaction with DFT calculation. It showed that both Si and N removal was difficult without F, while O removal was possible even without F. Thus, we determined that Si_3N_4 etching was more F-limited than Ox, indicating that selectivity at high C/F ratio gas would be improved. Based on all findings, We concluded that using the plasma with high C/F ratio radical helped to increase selectivity by protecting Si_3N_4 more with denser and harder FC film but not on SiO_2 due to the O-C bonds in formed FC film. This study will help to understand the fundamental behavior of the dielectric selectivity with various C/F ratio plasmas during the q-ALE process and ultimately provide the guideline for the experiment.

11:45am **ALE-TuM-16 Selecting a Method for ALE Modeling***, Y. Barsukov, S. Jubin, S. Ethier,* ***Igor Kaganovich,*** Princeton University Plasma Physics Lab

Several methods can be used for modeling dry etch processes, such as transition state theory (TST), classical and ab-initio molecular dynamics (MD), and density functional based tight binding (DFTB) approaches. The combination of TST and quantum chemistry methods, usually DFT (density function theory), enables the calculation of rate constants for the elementary steps of gas-surface reactions during the etching process. This allows insight into the etching mechanism, and we can then perform chemical kinetics modeling to predict the etch rate as a function of gas phase species fluxes and surface temperature. One limitation of the TST approach is the evolution of the structure and composition of the surface during the etching process, which results in a change in the rate constants. The purpose of chemical kinetics modeling is to find the rate-limiting step in surface reactions that determines the overall rate of the whole etching process. Here we present simulation results explaining the orientation dependence of silicon surface etching by F2 molecules using the TST approach. Namely, we show that the Si etching in the (111) direction is much slower than in the (100) and (110) directions; therefore, F2 can be used for the anisotropic etching process to produce black silicon. Moreover, this approach allows us to propose a new reactant to etch silicon with higher anisotropy. Among the other methods, classical and ab-initio MD simulations enable the study of surface transformation during the etching process, as well as the dynamics predicting surface composition and structure. However, great care must be taken when choosing the interatomic potentials for classical MD and the semi-empirical parameters for DFTB in order to correctly represent the surface reactions and their rates. Our simulations showed that bond order MD potentials unrealistically described boron adsorption on a graphene sheet, and available DFTB parameters sets were unable to predict the existence of NH4F and NH5F2 salts, which are broadly used for SiO2 and Si3N4 etching. The ab-initio MD method completely avoids these issues but is so time-consuming that simulating surface reactions proceeding through significant barriers can become prohibitively long. Nevertheless, it can be successfully used for studying barrier-free reactions or reactions with low barriers, such as SiO2 and Si3N4 etching by NH4F and NH5F2 salts. Thus, the selection of suitable modeling methods allows our group to simulate etching and identify key processes. These methods can be used for optimization of process parameters in designing new etchants.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE1-TuA

Plasma and Energy-Enhanced ALE

Moderators: Paul Abel, Tokyo Electron America, Inc., Dr. Dmitry Suyatin, Lund University

1:30pm **ALE1-TuA-1 In-Situ Analysis of Surface Reactions on Thin Films in Plasma-Assisted Thermal-Cyclic Atomic Layer Etching***, **Kazunori Shinoda**, N. Miyoshi, H. Kobayashi,* Hitachi, Ltd., Japan*; M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan **INVITED**

Isotropic atomic layer etching (ALE) is a conformal etching technique based on the sequential reactions of surface modification and desorption of the modified surface. Isotropic ALE may play a significant role in the manufacturing of next-generation 3D devices such as lateral gate-all-around (LGAA) FETs. Significant efforts are currently underway to develop and commercialize isotropic ALE for various thin-film materials utilized in semiconductor device manufacturing. The authors have developed a new approach for isotropic ALE called plasma-assisted thermal-cyclic ALE, which is based on the cycles of plasma exposure for surface modification and infrared heating for fast desorption of the modified surface. This approach offers a high degree of controllability in material selectivity because it uses two different temperatures for the modification step and desorption step. For example, the selectivity of W and TiN can be changed from highly selective to nonselective by tuning the infrared heating time, since heating at low temperature results in desorption of only the modified surface of W while heating at high temperature results in the desorption of the modified layers of both W and TiN. The two key reactions of plasma-assisted thermal-cyclic ALE are the formation and desorption of ammonium salt-based modified layers on nitride films. Conformal selective ALE of Si_3N_4 and TiN has been demonstrated by utilizing the ammonium salt-based reactions with hydrofluorocarbon-based plasmas. Highly selective ALE of nitride films over other films such as SiO_2 and poly-Si can be obtained because ammonium salt-based modified layers form only on nitride films. Selective ALE of SiGe over Ge was also demonstrated by using nitrogen-containing hydrofluorocarbon-based plasmas. One possible mechanism of the ALE of SiGe is the formation of an ammonium salt-based modified layer on SiGe. A new 300-mm etching tool, dry chemical removal (DCR), that features an inductively coupled plasma (ICP) source and infrared lamps, has been developed to enable rapid thermal-cyclic reactions. Selective ALE of a variety of materials including Si_3N_4, SiO_2, TiN, W, Co, and SiGe is possible using the DCR tool. This paper reviews the development of plasma-assisted thermal-cyclic ALE, places this development in the historical context, provides detailed information on surface reactions during ALE by *in-situ* x-ray photoelectron spectroscopy, clarifies the effects of surface oxides on surface reactions, and reports the latest results for atomic layer reactions on TaN.

2:00pm **ALE1-TuA-3 Isotropic Atomic Layer Etching Process for HfO_2 Film***, J. Kwon, C. Kim, **Byung Chul Cho**, J. Park, S. Park, J. Chun,* Semiconductor R&D Center, WONIK IPS Co., Ltd., Republic of Korea

The atomic layer etching (ALE) process is a sub-nanometer scale removal technique base on sequential, self-limiting surface reactions.[1,2] In this study, we developed a cyclic isotropic plasma ALE process that involves fluorination with NF3 plasma and ligand exchange with dimethylaluminumchloride (DMAC) for hafnium oxide (HfO_2). The HfO_2 surface is converted to HfOFx by NF3 remote plasma in the fluorination step, and the fluorinated layer is removed by a ligand exchange reaction with DMAC in the removal step. The ALE process was analyzed by ellipsometry, atomic force microscopy, dynamic secondary ion mass spectrometry, transmission electron microscopy, x-ray diffraction. Etching was not observed at 200 °C and was increased from 1.41 Å/cycle to 2.22 Å/cycle as the process temperature increased from 250°C to 300°C. Isotropic removal of HfO2 thin films was observed on the trench patterns with an aspect ratio of >15. In addition, the ALE process decreased the surface roughness of the HfO2 thin films.

2:15pm **ALE1-TuA-4 Thermal Atomic Layer Etching of CoO by an "Oxidation-Reduction" Mechanism Using Sequential Reactions of Ozone and Acetylacetone***, **Aziz Abdulagatov**, J. Partridge,* University of Colorado at Boulder*; V. Sharma,* ASM Microchemistry Ltd., Finland*; J. Murdzek, A. Cavanagh, S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of CoO was demonstrated using sequential exposures of ozone (O_3) and acetylacetone ($CH_3COCH_2COCH_3$, Hacac). Hacac can form volatile $Co(acac)_2$ complexes. Ozone was employed to remove carbon residue resulting from Hacac adsorption. *In situ* spectroscopic ellipsometry (SE) observed a linear decrease in CoO film thickness versus O_3 and Hacac exposures with etch rates of 0.09 and 0.43 Å/cycle at 200 and 250 °C, respectively. The O_3 and Hacac surface reactions were also found to be self-limiting.

The sequential O_3 and Hacac exposures were also observed to cause changes in oxidation state and crystal structure. X-ray diffraction (XRD) analysis of the as-deposited CoO thin films showed mostly hexagonal crystal structure. After O_3 exposures, XRD studies observed that hexagonal CoO was oxidized to cubic Co_3O_4. After ALE ending with Hacac exposure, XRD analysis also showed that the film was converted to cubic CoO. These XRD results indicate that Hacac can reduce Co_3O_4 back to CoO. In agreement with the thin film studies, XRD studies on Co_3O_4 powder observed the reduction of cubic Co_3O_4 to cubic CoO after Hacac exposures. X-ray photoelectron spectroscopy (XPS) analysis was also consistent with oxidation of CoO to Co_3O_4 by O_3 and the reduction of Co_3O_4 back to CoO by Hacac.

Quadrupole mass spectrometry (QMS) measurements observed $Co(acac)_2$ etch products during the Hacac exposures on CoO or Co_3O_4 powder. The observation of combustion products, such as CO_2 and H_2O, during Hacac exposures on Co_3O_4 powder was also consistent with the reduction of Co_3O_4 to CoO. The XRD, XPS and QMS results reveal alternating oxidation and reduction reactions during the O_3 and Hacac exposures that define this CoO thermal ALE process. The sequential reactant exposures that result in volatile release of $Co(acac)_2$ etch products occur concurrently with changes in the oxidation state and crystal structure of the underlying cobalt oxide.

2:30pm **ALE1-TuA-5 Surface Modification with Neutral Gas Cluster Beams and Its Application to Atomic Layer Etching***, **Noriaki Toyoda**, H. Tanaka, M. Takeuchi,* University of Hyogo, Japan

We have reported that halogen-free ALE can be performed on various metal films at room temperature using gas cluster ion beams (GCIB) and organic acids. However, GCIB system requires large vacuum pumps and high voltage power supplies. Even worse, throughput of GCIBs is relatively low, which limits the variety of applications.

We investigated the possibility of ALE using neutral cluster beams. Neutral cluster beams have a simple apparatus configuration and can be expected to enhance surface reactions by directional energy beams (total energy of about several hundred eV). In this study, the surface condition after neutral cluster beam irradiation was evaluated by XPS, and the etching depth after pseudo-ALE was investigated.

First, Ni film surface was cleaned by 500 eV Ar^+ irradiation, and then the substrate was irradiated with a neutral O_2 cluster beam for 300 s at a substrate temperature of 150 °C. After irradiation, the results were evaluated by XPS. NiO peak appeared around 860 eV in the Ni film on the O_2 cluster beam axis. On the other hand, NiO is not formed in the Ni film not irradiated by O_2 cluster beam, and Ni oxidation does not occur with residual oxygen. This indicates that the Ni oxide film can be formed by neutral O_2 cluster beam irradiation at a temperature where oxidation by the residual oxygen gas not occur.

Quasi-ALEs were performed by repeating O_2 neutral cluster beam irradiation on Ni films at 150°C and subsequent oxide film removal with acetic acid. At the on-axis position of O_2 neutral cluster beam, EPC was 1.6 nm. On the other hand, there was no measurable etching depth for the Ni film located at off-axis position. These results indicates that neutral cluster beam irradiation can be used for novel method for directional ALE.

2:45pm **ALE1-TuA-6 Development Plasma-Based Atomic Layer Etching of Zinc Oxide by Using Tetrafluoromethane Plasma and Dimethylaluminum Chloride***, **Chien-Wei Chen**, C. Chang,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan*; Y. Jhang,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Hsinchu, Taiwan

In recent years, atomic layer etching (ALE) has been proposed to be introduced into advanced semiconductor processes, especially in gate-all-around (GAA) or nano-sheet FET structures, due to its precision control and high selective ratio etching characteristics. Therefore, ALE processes for various thin-film materials are being developed with great enthusiasm. In this study, we achieved plasma ALE verification of ZnO thin films using tetrafluoromethane (CF_4) plasma and dimethylaluminum chloride (DMAC) as the precursors. The entire ALE reaction was performed on a 6" cluster ALE system (Fig.1) developed by Taiwan Instrument Research Institute (TIRI). We first deposited about 87 nm thick polycrystalline ZnO films with

ALD at 200°C, and then performed a total of 50 fluorinations of the ZnO films with a remote CF_4 plasma at a frequency of 10 s/cycle, and then performed *in-situ* XPS analysis. From Fig. 2a, it can be seen that the peak of Zn 2p 3/2 shifts from 1023.8 eV (Zn-O) to the stronger binding energy of 1024.4 eV (Zn-F) on the surface of the ZnO film after treated with CF_4 plasma, and a significant F1s signal appears (Fig. 2b). After confirming that the CF_4 plasma could achieve the ZnO surface fluorination modification, we added DMAC for the fluoride removal half-reaction. The complete process sequence was first to pass CF_4 gas to stabilize the chamber pressure at 0.5 Torr, then 50 W RF power was applying to trigger CF_4 plasma for 10 s, followed by passing LN_2 to remove the residual CF_4 gas, and then passing DMAC to remove the fluoride on the surface of ZnO film. DMAC is then passed through the chamber to purge the residual CF_4 gas, followed by DMAC pulsing for 0.1 s and soaking for 1 s to remove the volatile fluoride formed on the ZnO surface, and finally LN_2 is passed through to remove the residual DMAC to complete a complete ALE cycle. We also established the etching curve of ZnO ALE in Fig. 3, and it can be estimated that the etching per cycle (EPC) of ZnO ALE at 400°C is about 5.5 Å. In addition, we also observed in the subsequent TEM image analysis that the etched polycrystalline ZnO films in this ALE method will form porous ZnO films after a certain number of ALE cycles, which is presumed to be related to the crystal boundary of ZnO, and we will conduct more research on this characteristic in the future.

3:00pm **ALE1-TuA-7 Resistive Capillary Array Calorimetry Method for ALD and ALE Processes***, **Anil Mane**, J. Elam,* Argonne National Laboratory, USA **INVITED**

Calorimetry is an essential analytical technique for determining the thermodynamics of chemical reactions. In-situ calorimetry during atomic layer deposition and etching (ALD/ALE) processes would be a valuable tool to probe the surface chemical reactions that yield self-terminating growth and removal of material at the atomic scale. Besides this, in-situ calorimetry would reveal the partitioning of chemical energy between the individual half-reactions that constitute the ALD or ALE cycle. Here we present a calorimetry strategy that utilizes the temperature-induced resistance changes in ALD thin films. Our calorimetry approach utilizes an ALD nanocomposite resistive thin film deposited conformally on the inner surfaces of microcapillary array substrates. These substrates are fabricated using borosilicate glass capillaries, 3D-printing, or through-substrate interposers. The ALD nanocomposite layer has a high resistivity and a well-defined thermal coefficient of resistance (TCR), both of which can be fine-tuned by adjusting the nanocomposite layer composition via ALD process parameters.

In practice, the resistive capillary array (RCA) calorimeter is installed in the ALD system and electrically biased to produce a current that is recorded in real time. During the ALD/ALE surface reactions, heat exchanged with the coating produces transient current features due to the non-zero TCR of the nanocomposite resistive layer. These transient features are highly reproducible and can be used to calculate the reaction enthalpies of the individual surface reactions based on the TCR value and the thermo-physical properties of the capillary array substrates.

To demonstrate the RCA calorimetry method, we performed in-situ calorimetry measurements for a range of ALD processes including Al_2O_3, AlF_3, $Al_xO_yF_z$, ZnO, MgO, TiO_2, and ZrO_2 as well as ALE processes including Al_2O_3, TiO_2, MoS_2, and HfO_2. We also studied the nucleation behavior when transitioning between ALD processes and from ALD to ALE processes. We find good agreement between reported enthalpy changes for ALD reactions and the values measured by in-situ RCA calorimetry. We believe that RCA calorimetry is a versatile in situ method to study the thermodynamics of ALD/ALE surface reactions and a convenient diagnostic for real-time ALD/ALE process monitoring in a manufacturing environment. Briefly, we will also discuss the challenges and limitations of RCA calorimetry method.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE2-TuA

Low-Temperature and SiN ALE

Moderator: Dr. Kazunori Shinoda, Hitachi, Ltd.

4:00pm **ALE2-TuA-11 Atomic Layer Etching at Cryogenic Temperature***, **Thomas Tillocher**, G. Antoun, J. Nos,* GREMI CNRS/Orleans University, France*; C. Cardinaud, A. Girard,* IMN CNRS/Nantes University, France*; P. Lefaucheux, R. Dussart,* GREMI CNRS/Orleans University, France **INVITED**

Atomic Layer Etching (ALE) has been extensively studied for various materials these last years for microelectronic processes where high precision is required. Since cryogenic etching processes show interesting features, such as reduced reactor wall contamination, damage-free etching, enhanced surface residence time, ALE can benefit from cooling the substrate to cryogenic temperature (“Cryo-ALE”). Two approaches for Cryo-ALE have been developed and studied at GREMI for SiO_2, Si and Si_3N_4 and are presented in this paper.

Typically, ALE of SiO_2 is performed at room temperature and involves a C_4F_8 plasma in the modification step, which leads to some fluorocarbon deposition on the reactor walls, and eventually to process drifts. This can be addressed by flowing C_4F_8 in gas phase above the SiO_2 substrate cooled at cryogenic temperature. Under such conditions, species are physisorbed only at the cooled surface and therefore, wall pollution is suppressed. It is shown that repeating cycles of a C_4F_8 physisorption step followed by an Ar plasma with low energy ion bombardment, each separated by a purge step, makes it possible to sequentially etch SiO_2. Cryo-ALE of SiO_2 using C_4F_8 has proved successful results at -120°C and 3 Pa. However, no etching is observed at -110°C, since C_4F_8 does not significantly physisorb at such a temperature. In this paper, the role of the surface temperature on physisorption and the surface residence time is discussed by means of quasi in-situ XPS, mass spectrometry and in-situ ellipsometry.

In the second process presented in this paper, C_4F_8 physisorption is replaced by a SiF_4/O_2 plasma, with the substrate still cooled at low temperature. A SiO_xF_y layer is deposited at each cycle and acts as a fluorine reservoir used to etch the substrate when exposed to a low energy ion bombardment in an Ar plasma. It is shown that the process switches from a deposition regime at room temperature to an etching regime at low temperature. The threshold temperature, which is material dependent (-65°C for Si_3N_4 and -100°C for Si), is related to the deposition of a much thicker and more fluorinated SiO_xF_y layer. Therefore, there is a narrow temperature window in which it is possible to etch Si_3N_4 selectively to Si by ALE. This will be further discussed with in-situ ellipsometry measurements and quasi in-situ XPS analyses.

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4:30pm **ALE2-TuA-13 SiO_2 ALE based on High Boiling Point Fluorocarbon Physisorption***, **Dain Sung**, G. Yeom, H. Tak, D. Kim,* Sungkyunkwan University, Republic of Korea

SiO_2 atomic layer etching (ALE) using fluorocarbon plasmas as adsorption process is currently investigated to etch silicon dioxide for self-aligned contact (SAC) etch process of logic devices due to various benefits such as high etch selectivity over silicon nitride, low aspect ratio dependent etching (ARDE), low surface damage, controlled etching, etc.However, for conventional SiO_2 ALE utilizing fluorocarbon plasmas, a drift in etch process through cycles could be induced by chamber contamination caused by dissociated fluorocarbon radicals during the plasma generation. To avoid chamber contamination by fluorocarbon radicals, adsorption of fluorocarbon gases instead of generation of fluorocarbon plasmas by using cryo etching technique is also currently investigated, however, it requires extremely low substrate temperature facilities, etc. To overcome these challenges, ALE based on high boiling point PFC physisorption in low substrate temperature as the fluorocarbon adsorption is proposed as an alternative process. In this study, 100nm Si_3N_4 line masked SiO_2 was etched in an ICP etch system and high boiling point (HBP) PFC was used as a precursor during the physisorption step. When the substrate was cooled at 0°C and -10°C, HBP PFC molecules were adsorbed on SiO_2 and Si_3N_4 because it has boiling point higher than room temperature. After purging step, the etching step is achieved by using Ar plasma with a low energy ion bombardment. After the ALE process, ellipsometry and field emission scanning electron microscopy (FE-SEM) were used to analyze the etch properties such as etch rate, etch selectivity, and etch profiles of SiO_2. Compared to C_4F_8 plasma ALE, physisorption ALE using HBP PFC exhibited higher SiO_2 etch selectivity over Si_3N_4 in addition to no contamination of chamber walls.

4:45pm **ALE2-TuA-14 Cryogenically Cooled, Saturating Quasi-ALE of Silicon Nitride***, **Frank Greer**, D. Shanks, R. Ahmed, J. Femi-Oyetoro, A. Beyer,* Jet Propulsion Laboratory (NASA/JPL)

Silicon Nitride is one of the most important materials used in photonic integrated circuits. Anisotropic Plasma Atomic Layer Etching (ALE) is well known for its inherent advantages of uniform, precise, and smooth etching of materials. These features may make the technique attractive for waveguide etching to reduce sidewall losses. However, there are some important limitations of a truly atomic layer-by-atomic layer etching approach. Waveguides can be ~800nm thick, making sub-nanometer etch rates per cycle (EPC) substantially slower than conventional ICP and RIE etching processes. Although there are reported approaches that enable higher EPC, the process conditions cited are difficult to repeat in a standard ICP etching chamber due to the high process pressures utilized.[1] Additionally, some materials, like silicon nitride, do not have plasma chemistry that naturally divides into saturating reaction and desorption steps with high ALE synergy.[2]

In this work, we have leveraged cryogenic substrate temperatures to dramatically enhance the ALE synergy of silicon nitride etching for films from two different LPCVD silicon nitride deposition recipes. Our cyclic Cryo-ALE process utilizes a simple gas chemistry involving H2, SF6, and Ar where a biased hydrogen implantation dose step creates a chemically modified damage layer, that is removed by a gentle SF6/Ar ICP etch step. ALE synergy dramatically improves as substrate temperature is reduced because cryogenic temperatures largely quench the spontaneous etching caused by fluorine radicals. At 10C, ALE synergy is ~30%, but increases to as high at 70% at -50C. As expected, saturating behavior for EPC is improved in the SF6 step at low temperature. Additionally, cryo-temperatures are accompanied by smoother etched surfaces. As with the previous report for quasi-ALE of silicon nitride, our cryo-ALE process EPC can be controlled precising by tuning the bias voltage of the hydrogen implantation step. Surprisingly, however, despite the high degree of ALE synergy and the nearly identical silicon to nitrogen ratio of the two LPCVD films, the etch profile was very different, showing that the hydrogen content of the as-deposited film and/or the density also plays a role.

These results suggest that the combination of creating a chemically modified damage layer with cryogenic etching temperatures may be a general approach to simultaneously increase EPC and ALE synergy for fluorine-based etching of materials. Opportunities to generalize this approach and silicon nitride device data will also be discussed.

1 Sonam D. Sherpa *and* Alok Ranjan JVST A **35**, 01A102 (2017)

2 Akiko Hirata *et al* 2022 *Jpn. J. Appl. Phys.***61** 066002

5:00pm **ALE2-TuA-15 High Throughput SiN ALE and Its Damage Control***, **Akiko Hirata**,* Sony Semiconductor Solutions Corporation, Japan **INVITED**

The miniaturization of semiconductor devices has almost come to an end, but the combination of 3D devices / 3D structures, miniaturization, and new materials continues to meet market demands. Dry etching technology using plasma is one of the most important processes in achieving this performance improvement. In particular, processing technology at the atomic/molecular level is required to realize device shrinkage and dimensional control of several nm is indispensable for manufacturing cutting-edge devices. Atomic Layer Etching (ALE) can realize high-precision etching, however, has the issue of long processing time. In the conventional ALE (conv.-ALE), the low ion energy is used to realize the self-limited reaction at the atomic level. Self-limiting process means the extremely high-selective etching of a modified layer over the pristine substrate. One ALE cycle consisted of a surface modification step and a removal step of the modified layer. In the modification step, the binding energy in the surface reactive layer is weakened so that it is easier to remove than the bulk. ALE was performed by irradiating Ar ion for a long time.

In this study, we focused on SiN ALE [1]. We verified the feasibility of high-throughput ALE (HT-ALE). To reduce the time, we performed HT-ALE with high ion energy and evaluated the amount of etched SiN. SiN HT-ALE for short time with high ion energy exhibited a quasi-self-limited reaction, which is a characteristic of ALE, and the processing time could be reduced by 1/5th. To further analyze HT-ALE with varying energy in the desorption step, the energy required to remove the reaction layer was calculated. The amount of etching in the reaction layer was determined by the number of Ar ions, incident energy considering IEDF, energy loss in the polymer, and process time. Next, the interface trap density values after conv.-ALE and HT-ALE were performed for damage evaluation. However, HT-ALE using CH_3F in the adsorption step exhibited signs of increased damage due to ion injection with high energy. The HT-ALE has a deeper H penetration depth and a deeper Si damage layer than the conv.-ALE from the surface analysis. Thus, C_4F_8 that does not contain H can significantly reduce the damage, even in HT-ALE conditions. Damage is generated by the knock-on effect of H, which has a small atomic weight. H-less HT-ALE achieves both damage-less and high throughput. To alleviate the issue of long ALE processes, it is important to precisely control the ion energy/flux, process time, and damages.

[1]Hirata, A., Fukasawa, M., Kugimiya, K., Karahashi, K., Hamaguchi, S., Hagimoto, Y., and Iwamoto, H.,*Japanese Journal of Applied Physics* **61**, SI1003 (2022).

5:30pm **ALE2-TuA-17 The Atomic Layer Etching Database: A Valuable Crowd-Sourced Platform for the Community***, N. Chittock, A. Mackus, H. Knoops, B. Macco, **Erwin Kessels**,* Eindhoven University of Technology, The Netherlands

In this contribution, we will introduce the ALE database (DOI:10.6100/aledatabase [https://www.atomiclimits.com/aledatabase/]) which is free of charge available on the AtomicLimit.com blog site. It was established after launching the ALD database (DOI: 0.6100/alddatabase [https://www.atomiclimits.com/alddatabase/]) in 2019. The latter has become very popular in academia and in industry and it has appeared in many presentations and publications in recent years. It has also been used as a starting point in review papers, for example by applying data analytics. We hope that a similar thing will happen to the ALE database in order to serve the ALE community.

The ALE database displays all ALE process reported in the literature in the format of the periodic table. It distinguishes between anisotropic ALE processes and isotropic ALE processes. By clicking on an element in the periodic table, a list of materials containing that element is displayed as etched by an ALE process. The etchants species are listed per ALE process and there is also a direct link to the publications in the literature. The ALE database been compiled from the data in the literature and new processes can be added by visitors of the website. This means that it stays up to date by crowd-sourcing. Authors of ALE papers are stimulated to add their ALE processes to the database.

In the presentation, the features of the ALE database will be highlighted and also some scientific trends will be discussed as can be inferred from the data in the ALE database. Also the possibilities for data mining will be addressed and potential future extensions (relying on contributions from the community) will be discussed. The intention is to make the ALE database an even more valuable platform for the ALE community.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE1-WeM

Si and SiO_2 ALE

Moderators: Prof. Austin Minnich, Caltech, Prof. Gregory N. Parsons, North Carolina State University

8:00am **ALE1-WeM-1 Plasma-Enhanced Atomic Layer Etching for Metals and Dielectric Materials***, **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. Atomic layer etching (ALE) processes are being actively studied and developed for various semiconductor and dielectric materials as well as metals. In this talk, various plasma-enhanced ALE (PEALE) processes will be discussed for isotropic and anisotropic patterning of metals and dielectric materials such as molibdenum, ruthenium, cobalt, titanium nitride, tantalum nitride, halfnium oxide, zirconium oxides. [1-6] Typical ALE processes consist of surface modification step and removal step. For the surface modification, various fluorination, chlorination and oxidation schemes were applied including fluorocarbon deposition, halogenation, oxidation with radicals generated plasmas. For the removal or etching step, various schemes were applied including ion-bomardment, heating, ligand volatilization, ligand exchange, and halogenation. The surface characteristics and requirements of plasma-enhanced ALE will be also discussed.

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2) Y. Cho, Y. Kim, S. Kim, H. Chae, *J. Vac. Sci. Technol. A*, 38(2), 022604 (2020)

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4) D. Shim, J. Kim, Y. Kim, H. Chae, *J. Vac. Sci. Technol. B.*, 40(2) 022208 (2022)

5) Y. Lee, Y. Kim, J. Son, H. Chae, *J. Vac. Sci. Technol. A.*, 40(2) 022602 (2022)

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8:30am **ALE1-WeM-3 Controlling the Hole Profile of High Aspect Ratio Structures in Atomic Layer Etching of SiO2 by Utilizing Dc-Superposition in Capacitively Coupled Plasmas***, **Kang-Yi Lin,** E. Hirsch, P. Wang,* TEL Technology Center, America, LLC, USA

As semiconductor manufacturing advances to nanometer scale processing nodes, the development of contact and via in middle-of-line (MOL) and back-end-of-line (BEOL) schemes continuously shrinks critical dimension (CD) with higher aspect ratio structures. The etching process faces the demand for better control of the profile, including taper angle and the etching selectivity of SiO_2 to the mask and etch stop layer. Conventional approaches, such as continuous-wave plasma, using a mixture of etchants and passivation precursors for selective removal undergo the bottleneck as the feature moves to the nanometer scale. Aspect ratio-dependent transportation impedes the processing window to meet the criteria on etching profile and selectivity. Atomic layer etching (ALE) is an emerging approach that separates the surface functionalization and etching byproduct activation steps to enable selective removal in a self-limited fashion and to mitigate aspect ratio-dependent etching. Our capacitively coupled plasma (CCP) etcher enables a feature that imposes a negative direct current (DC) bias on the top electrode, which attracts ions for sputtering reactions and produces Si deposition and ballistic secondary electrons to the bottom electrode. We studied the effect of DC-superposition (DCS) in CCP under an ALE sequence on the hole profile, including the coating thickness on the substrate, the thickness loss of the mask and etch stop layer, and the etching profile. Other surface characterization methods, including x-ray photoelectron spectroscopy (XPS), were used to understand the surface evolution of each step during the ALE sequence. Experimental results show that DCS can be used to control the etching selectivity and taper angle. The optimal condition delivers a vertical taper angle close to 90° on the etch stop layer with neglectable mask losses. Exploiting DCS in an ALE sequence under CCP offers a novel processing window to improve etching profiles in the nanometer scale feature.

8:45am **ALE1-WeM-4 Damage Analysis of Reactive Ion and Quasi-Atomic Layer Etched Silicon***, A. Karimi,* AlixLabs AB, Sweden*; M. Alabrash,* Lund University, Sweden*; R. Jafari Jam,* AlixLabs AB, Sweden*; D. Lishan,* Plasma-Therm LLC*; H. Aslan, J. Garnæs,* Danish Fundamental Metrology, Denmark*; A. Uvarov,* Plasma-Therm Europe, France*; Y. Ilarionova,* ***Dmitry Suyatin****, J. Sundqvist,* AlixLabs AB, Sweden*; S. Khan,* Danish Fundamental Metrology, Denmark*; I. Maximov,* Lund University, Sweden

Atomic layer etching (ALE) is a cyclic technique based on self-limiting processes, such as reactive gas adsorption and material removal by low-energy ion bombardment. In a typical ALE process Ar^+ ions with energies of 20-60 eV are used to desorb the reaction products, e.g. $SiCl_x$ for the Si ALE. Compared to a corresponding continuous reactive ion etching (RIE), where the ion energies often exceed 100 eV, the ALE should yield less surface damage due to low ion energy and its cyclic nature. However, there are few publications only dealing with studies of the surface damage in ALE.

For Si etching experiments with Cl_2 and Ar as etch gases, we used a commercial Inductively Coupled Plasma RIE Takachi™ tool from Plasma-Therm LLC. The system was operating in a quasi-ALE (Q-ALE) regime with some RIE contribution during the removal step due to residual Cl_2. In order to avoid surface contamination by lithographic masks, a custom-made metal shadow masks were used to protect some Si areas from the Ar^+ ion bombardment. The Kelvin Probe Force Microscopy (KPFM) measurements were then performed both on the reference and the etched places to calculate the contact potential difference (CPD) values for the RIE and Q-ALE samples.

Here we present our results on application of KPFM to evaluate the surface damage of Si for both Cl_2/Ar-based RIE and Q-ALE processes. We used two methods for chlorinating the Si surface: a) molecular chlorination where plasma was only ignited during the Ar^+ etching step and b) plasma chlorination where plasma was ignited during the entire process and pulsed during etching step. The KPFM is used to measure the CPD between the etched Si surface and the tip and this potential difference reflects the surface damage. At the same time, a surface morphology was also characterized in an atomic force microscopy mode. Both the CPD and the surface roughness are used to evaluate the damage after cyclic ALE processes at different RF-bias power. The results were then compared with a sample that had undergone RIE in order to provide a comprehensive evaluation of the impact of the etching process on the surface morphology of the samples.

We present and discuss the CPD and surface roughness data as a function of bias voltages for both RIE and Q-ALE. The experimental results in this study show that the CPD of Si after the Q-ALE processes are in close proximity to the theoretically calculated value. However, if the samples are subjected to continuous RIE with the same parameters, the surface potential deviates significantly from the theoretical value. This may indicate that the Q-ALE process gives a significantly lower damage of Si compared to a standard RIE.

9:00am **ALE1-WeM-5 Atomic Layer Etching of SiO_2 via H_2/SF_6 Plasma and TMA***, **David Catherall,** A. Minnich,* California Institute of Technology

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

9:15am **ALE1-WeM-6 Learnings and Mitigations of Nonuniformity in Oxide Quasi Ale Applied to Contact Patterning***, **Francois BOULARD,** A. RONCO, N. POSSEME,* CEA/LETI-University Grenoble Alpes, France

Ideal Atomic Layer Etching (ALE) with truly self-limited half cycle offers many advantages to conventional etching processes. The independent control of the modification and the removal steps offers higher etch selectivity, could smooth surfaces, or minimizes the dependence to aspect ratio and wafer location [1]. However, in oxide quasi ALE based on FluoroCarbon (FC) plasma, where a thin FC film is deposited, self-limitation is not obvious. In such circumstance, the return to a pristine surface between cycles is no longer guaranteed and the Etch Per Cycle (EPC) or surface roughness become very sensitive to process conditions [2]. Moreover, in a throughput perspective, the removal step should be shortened as much as possible, stressing even more the process window. In this paper, we present recent experimental results obtained on 300 mm blanket and contact patterned SiO_2 etch. A multi-frequency capacitively coupled plasma with C_4F_6/Ar chemistry is used. A particular attention is paid to the wafer uniformity of deposition and removal activation. We analyze the impacts of deposition and activation times on the EPC and roughness uniformities. We show how intentional nonuniform deposition and removal half cycles could help to optimize the quasi ALE process. Finally, we apply these understandings on contact etching for Si qubits and FDSOI advanced nodes technologies with stringent soft landing requirements.

[1] K.J. Kanarik, et. al., J. Vac. Sci. Technol. A **35**, 05C302 (2017)

[2] X. Wang, M. Wang, P. Biolsi, and M. J. Kushner, J. Vac. Sci. Technol. A **39**, 033003 (2021)

9:30am **ALE1-WeM-7 Adopting a Low Global Warming Potential Fluorocarbon Precursor (C_6F_6) to Atomic Layer Etching of Sio₂ with Fluorocarbon Plasmas**, ***Inho Seong**, Y. You, Y. Lee,* Chungnam National University, Republic of Korea*; G. Yeom,* Sungkyunkwan University, Republic of Korea*; S. You,* Chungnam National University, Republic of Korea

Reducing the greenhouse effect induced in plasma etching with the use of greenhouse gases such as CF_4 and C_4F_8 have been attracting enormous interests in the industry and academia. In SiO_2 atomic layer etching (ALE) with fluorocarbon plasma, we adopt an alternative precursor, C_6F_6, that has been known to have significantly low global warming potential, for gas mixtures with CF_4 and C_4F_8, which is one of the most widely used precursors while has a high GWP. The ALE results obtained with different gas chemistry are monitored by in situ ellipsometry and their ALE characteristics such as self-limiting behaviors are discussed in this paper. We expect this result to provide an opportunity for low global warming potential precursors to be adopted more widely in the etching process.

9:45am **ALE1-WeM-8 Thermal ALE Reactants for Semiconductor Processing**, ***Martin McBriarty,*** EMD Electronics

The devices that enable our digital future require clean, selective atomic layer processes to shape their complex 3-D nanoarchitectures. Isotropic ALE is a critical part of this toolkit, but each ALE process will be burdened with strict requirements for high selectivity and low levels of impurities and residues. Bringing such processes online requires ALE reactants that are not only effective, but also safe, sustainable, and readily integrated into the fab. Thermal ALE reactants from EMD Electronics are poised to meet these challenges. Etch performance and selectivity are efficiently tested using high-throughput process screening on 300mm ALE tools, followed by fab-grade physical and electrical characterization. For denser memory devices, we demonstrate ALE methods to shape high-*k* dielectrics which leave minimal residues without requiring the use of corrosive gases. For the interconnects and vias that tie together ever-shrinking transistors, we show ALE processes that selectively and precisely etch metals without compromising their electrical performance. The ALE processes discussed herein can be performed in the vapor phase, without requiring plasma generation, wet etch steps, or corrosive gas facilitization, enabling facile integration of isotropic ALE onto atomic layer processing tools.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE2-WeM

Plasma and Energy-Enhanced ALE

Moderator: Prof. Dr. Heeyeop Chae, Sungkyunkwan University (SKKU)

10:45am **ALE2-WeM-12 Isotropic Plasma-Thermal Atomic Layer Etching of Aluminum Nitride Using SF_6 Plasma and $Al(CH_3)_3$**, ***Austin Minnich,*** Caltech **INVITED**

We report the isotropic plasma atomic layer etching (ALE) of aluminum nitride using sequential exposures of SF_6 plasma and trimethylaluminum ($Al(CH_3)_3$, TMA). ALE was observed at temperatures greater than 200 C, with a maximum etch rate of 1.9 Å/cycle observed at 300C as measured using ex-situ ellipsometry. After ALE, the etched surface was found to contain a lower concentration of oxygen compared to the original surface and exhibited a ~35% decrease in surface roughness. These findings have relevance for applications of AlN in nonlinear photonics and wide bandgap semiconductor devices. [arXiv:2209.00150]

11:15am **ALE2-WeM-14 Gan Atomic Layer Etching Using SF_6 and Ar Plasmas Controlled by RFEA and Langmuir Probe Measurements**, ***Remi Dussart,*** Universite d'Orleans - CNRS, France*; L. Hamraoui, T. Zhang, A. Crespi,* Universite d'Orleans, France*; M. Boufnichel,* STMicroelectronics, France*; P. Lefaucheux,* CNRS, France*; T. Tillocher,* Universite d'Orleans, France

Chlorine based plasmas are usually preferred to etch GaN because of the formation of $GaCl_3$ molecules at the surface, which are quite volatile[1]. In fluorine-based plasmas, GaF_3 molecules are formed at the surface as well, but they are not volatile except at a very high temperature[1]. However, in atomic layer etching, SF_6 plasma can be used to control the etching at the atomic scale. Indeed, the Ga surface can be saturated of fluorine, producing a monolayer of GaF_x sites, which are supposed to not desorb during the modification step. Then, this modified layer can be sputtered selectively during the argon plasma removal step if the sputtering threshold of this layer is lower than that of GaN.

In this presentation, we would like to highlight the advantage of using probes such as ion Retarding Field Energy Analyzer (RFEA) and Langmuir probes to control the ALE process. With such plasma diagnostics, it is possible to evaluate the energy of the ions bombarding the surface and adjust theprocess parameters in order to avoid direct sputtering of GaN, and selectively remove the modified layer.

We used an Inductively Coupled Plasma (ICP) reactor excited at a frequency of 13.56 MHz with an RF generator to perform the experiments. The self-bias voltage was varied using an independent RF power supply operating at the same frequency. Experiments were performed at different source powers and different pressures of argon. This study led to an optimized etching process, which enables the control of the etching at the atomic scale, monolayer by monolayer. An energy scan was carried out and the synergy of the ALE process was evaluated. In certain ion flux conditions during the removal step with the Ar plasma, a self-limiting regime could be obtained.

In parallel, we used and adapted the global model developed by Pascal Chabert's team[2] at the "Laboratoire de Physique des Plasmas" in Palaiseau, France, to our reactor in order to simulate the plasma parameters for both Ar and SF_6 plasmas under different experimental conditions. Finally, some material characterization experiments (AFM, XPS, and ToF SIMS) were performed to analyze the GaN surface after the ALE process.

Acknowledgment

The authors appreciate the support provided by the European Union (IPCEI: Important Project of Commun European Interest) and Région Centre Val de Loire for the Nano2022 project. We also thank the CERTeM 2020 platform, which supplied the majority of the equipment.

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[2] C. Lazzaroni, K. Baba, M. Nikravech, and P. Chabert, J. Phys. Appl. Phys. **45**, 485207 (2012).

11:30am **ALE2-WeM-15 Speedy and Smooth Atomic Layer Etching for Silicon Carbide with DC Bias-Pulsing**, ***Julian Michaels,*** University of Illinois at Urbana-Champaign*; N. Delegan,* Argonne National Laboratory, USA*; Y. Tsaturyan,* University of Chicago*; R. Renzas,* Oxford Instruments*; D. Awschalom,* University of Chicago*; G. Eden,* University of Illinois at Urbana-Champaign*; J. Heremans,* Argonne National Laboratory

Atomic layer etching (ALE) is a cyclical process that shows promise for precisely fabricating nanostructures in a variety of materials. Silicon carbide (SiC) is a wide bandgap semiconductor material known for its excellent electrical, thermal, and mechanical properties. These properties make SiC a common material for power electronics, optoelectronics, and quantum optics. Conventional dry etching techniques for SiC suffer from poor selectivity, roughness, and damage the crystalline structure. ALE offers a solution to these shortcomings by utilizing self-limiting chemical reactions to remove individual atomic layers of SiC, resulting in precise etching that leaves smooth surfaces.

We present a novel execution of ALE for SiC using a bias-pulsing scheme and demonstrate self-limiting single dimer (i.e. the Si-C doublet) removal with an Ar/Cl2 inductively coupled plasma reactive ion etching (ICP RIE) system by only pulsing the plasma DC bias. Gases are not purged between etch steps, which leads to etch cycles of merely 6 seconds, which are far shorter than those of conventional ALE methods. Our results show that this ALE process can achieve precise etching with sub-angstrom surface roughness. We believe that this technique will enable new SiC-based quantum devices, especially those that are sensitive to surface quality, and that bias-pulsed ALE can be applied to other material systems to provide a more rapid solution for ALE.

11:45am **ALE2-WeM-16 Thermal Atomic Layer Etching of MoS_2 Films**, *J. Soares, **John Hues**,* Micron School of Material Science and Engineering, Boise State University*; A. Mane, D. Choudhury, S. Letourneau,* Applied Materials Division, Argonne National Laboratory*; S. Hues,* Micron School of Material Science and Engineering, Boise State University*; J. Elam,* Applied Materials Division, Argonne National Laboratory*; E. Graugnard,* Micron School of Material Science and Engineering, Boise State University

2D materials can offer promise for a wide range of application within semiconductor manufacturing. Of these materials, molybdenum disulfide (MoS_2) is of great interest due to its high mobility, measured on/off ratio, tunable band gap, and a film thickness ideal for scaling. In order to move this material closer to integration with semiconductor manufacturing, a great amount of processing control is required. Atomic layer processing techniques can accommodate this needed precision, where both the deposition and removal of MoS_2 has been studied. In this work we report a thermal atomic layer etching (ALE) process for MoS_2 using MoF_6 and H_2O as precursor reactants. Here, we will discuss atomic layer etching of both amorphous as-deposited and crystalline MoS_2 films. In situ quartz crystal microbalance measurements (QCM) indicate removal of as-deposited films when switching from a deposition chemistry (MoF_6 + H_2S) to the proposed etching chemistry (MoF_6 + H_2O). Saturation curves for the etching process were additionally identified with QCM by studying the mass gained per cycle versus the precursor dose duration. Films deposited on planar coupons were characterized with ellipsometry and X-ray reflectance to determine the etch per cycle. We propose the chemical reaction equations for the etch process as guided by residual gas analysis of byproduct formation, Gibbs free energy calculations, and QCM mass ratio analysis. After ALD and subsequent ALE processing, we produced few layer crystalline MoS_2 films once annealed. With the many application of both amorphous and crystalline MoS_2, this work helps to identify and expand current atomic layer processing chemistries.

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