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

ALE-SuP-1 Anisotropic Atomic Layer Etching of Sn by Formation of Hydride/Chloride*, **Doo San Kim**, Y. Jang, H. Gil, G. Yeom,* Sungkyunkwan University, Korea (Republic of)

Anisotropic ALE studies were conducted on Sn, which is one of the materials with a high extinction coefficient applicable to extreme ultraviolet (EUV) photo-lithography mask, by modifying the Sn surface with H/Cl radicals and followed by the removal of the modified layer by Ar$^+$ ions using an ion beam. During the adsorption of H/Cl radicals, it was possible to form highly volatile SnH_xCl_y and $SnCl_x$ without spontaneous etching on the Sn surface while the adsorption of H radicals etched the Sn surface by forming volatile SnH_x. The chemically modified $SnH_xCl_y/SnCl_x$ was etched by Ar$^+$ ions at ~2.6 Å/cycle through optimized ALE processes. In addition, high etch selectivity could be obtained with Ru which is generally used as a capping layer of the EUV photo mask. The degree of physical and chemical damages on the Ru surface was investigated during the adsorption and desorption of the Sn ALE process, and no physical and chemical damages could be found on the Ru surface during the Sn ALE process.

ALE-SuP-2 Atomic-Scale Control of a Native Oxide Thickness on Si for Direct Wafer Bonding*, **Youngseok Lee**, Y. You, C. Cho, I. Seong, W. Jeong, J. Lee, S. Kim, S. You,* Chungnam National University, Korea (Republic of)

Since direct wafer bonding technology has recently been attracting an enormous interest for three-dimensional integration of semiconductor devices, it has been reported that plasma treatment on wafer surfaces has advantages in, for instance, achieving high bonding strengths with low annealing temperature. We empirically found that in Si-SiO_2 bonding, a native oxide layer on Si plays an important role and thus a control of the native oxide thickness significantly affects the resulting bonding strength. In our experiments, physical sputtering of Ar plasma ions finely controlled a native oxide thickness of a Si wafer, and the change in the native oxide thickness and the resulting bonding strength with a SiO_2 wafer were assessed via ex situ ellipsometry and a double cantilever beam method, respectively. In this presentation, we will discuss the correlation between a native oxide thickness and bonding strengths and the underlying mechanism.

ALE-SuP-3 Atomic Layer Etching of Al_2O_3 with NF_3 Plasma Fluorination and Trimethylaluminum Ligand Exchange*, **Hyeongwu Lee**, J. Kim, D. Shim, Y. Kim, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

In this study, a cyclic isotropic plasma atomic layer etching (ALE) process for aluminum oxide was developed with two steps of plasma fluorination and ligand volatilization with trimethylaluminum (TMA). In the plasma fluorination step, the Al_2O_3 surface was fluorinated to $AlOF_x$ with NF_3 plasma at 100 °C. As the plasma fluorination time increased, the atomic fraction of fluorine on the surface was increased and then saturated to a value of 25% after 50s of plasma fluorination. The formation of the $AlOF_x$ layer was confirmed by X-ray photoelectron spectroscopy analysis. The depths of the fluorinated layers were in the range 0.79–1.14 nm at different plasma powers. In the removal step, the fluorinated layer was removed by a ligand exchange reaction with TMA at an elevated temperature range of 250–480 °C. The etch per cycle (EPC) was 0.20–0.30 nm/cycle and saturated after 30 s in the temperature range of 290–330 °C. EPC increased in the temperature range of 250–300 °C during the removal step with the ligand exchange reaction and reached the maximum at 300 °C. The fluorine atomic fraction on the surface was reduced to 14% after the removal. The average surface roughness of Al_2O_3 was reduced from 8.6 Å to 5.3 Å after 20 cycles of etching. In conclusion, Al_2O_3 was successfully etched at the atomic scale by the cyclic plasma ALE process.

ALE-SuP-4 Low-Temperature Plasma Atomic Layer Etching of Titanium Nitride*, **Heeju Ha**, D. Shim, J. Kim, Y. Kim, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

Titanium nitride (TiN) has been used as a metal gate electrode from 2D FinFETs to 3D FinFETs due to its proper mid-gap work function, high thermal stability, and excellent adhesion. Metal gates require a low-temperature process to prevent device degradation. Therefore, atomic-scale etching techniques at low temperatures are required for TiN films in 3D structures. In this work, plasma atomic layer etching (ALE) was developed for TiN using 3 steps of plasma oxidation, plasma fluorination, and thermal removal. In the plasma oxidation step, TiN was oxidized to form TiO_2 with O_2 plasma at 100℃. The TiO_2 thickness was saturated with O_2 plasma after an exposure time of 300s and saturated thickness increased from 0.29 to 1.23nm with increasing temperature and RF power. In the plasma fluorination step, TiO_2 layer was converted to TiO_xF_y with CF_4 plasma at 100℃. The F atomic percentage on the surface was saturated at 12% with RF power below 15W. In the thermal removal step, TiO_xF_y layer was completely removed above 150℃. The removal rate of TiN ranged from 0.24 to 1.71 nm/cycle by controlling the TiO_2 thickness determined earlier. The roughness of TiN surface decreased from 1.27nm to 0.26nm after 50 cycles of ALE process. The suggested TiN ALE process is expected to provide an effective process for atomic-scale three-dimensional structures.

ALE-SuP-5 Prediction of Chemical Evolution and Its Impact on PEALE of Silicon Nitride with Hydrofluorocarbons*, **Erik Cheng**, G. Hwang,* University of Texas at Austin*; P. Ventzek, Z. Chen, S. Sridhar, A. Ranjan,* Tokyo Electron America

Viable plasma enhanced atomic layer etching (PEALE) of silicon nitride (SiN) by inert ion bombardment of a hydrofluorocarbon (HFC) treated surface has been demonstrated, but the nature of the surface through HFC adsorption and SiN removal is poorly understood. A comprehensive first-principles based simulation investigation of this process suggests Ar$^+$ ion bombardment of an adsorbed HFC is accompanied by damage of the SiN and implantation of small H, F, and C containing fragments into the substrate. The quasi-equilibrium (QE) film structure is predicted to be associated with a significant density of coordination defects, an approximately half Gaussian distribution of H, F, C in the bombardment direction, and a stoichiometry determined by the HFC used. Model QE structures of appropriate structure and composition were then constructed based on the observed evolution of SiN films under simulated PEALD conditions. These structures were bombarded by argon ions to describe volatilization of the film. We find that F is critical for etch enhancement. A transition from etch initiation, through etch with emanation of nonequilibrium products, and then equilibrium products as a function of F load and ion energy is observed. The inhibiting or enhancing role of H and C load relative to F load is also demonstrated. Loading H instead of F is associated with minimal to no etch enhancement, whereas loading C results in the suppression of etch reactions from the formation of highly stable SiC.

ALE-SuP-6 Achieving High Uniformity in Atomic-Scale Etching via a Purgeless Atomic Layer Etching Approach*, **Yebin You**, Y. Lee, C. Cho, I. Seong, W. Jeong, J. Lee, S. Kim, Y. You, M. Choi, T. Yuk, S. You,* Chungnam National University, Korea (Republic of)

Since plasma had been employed to the etch process of semiconductor manufacturing, etch uniformity has been one of the most important issues, and in this atomic scale era, high etch uniformity is of increasing importance. In achieving atomic-scale uniformity, atomic layer etching (ALE) has arisen as a next-generation etch technique due to its self-limiting characteristic. The long processing time of ALE however hinders the wider employment of ALE in the semiconductor industry. In this presentation, we will propose a novel ALE method where no purging step is required and discuss its applicability with the evaluation of its ability to obtain high etch uniformity over a wafer-scale area.

ALE-SuP-7 Thermal Atomic Layer Etching of Tantalum Nitride With Plasma Surface Oxidation and Fluorination*, **Hojin Kang**, H. Chae, Y. Kim,* SKKU, Korea (Republic of)

Conventional copper (Cu) interconnect technology requires a diffusion barrier between Cu and dielectric structures because Cu diffuses rapidly in the dielectric.[1] Tantalum nitride (TaN) is one of the promising materials for Cu diffusion barrier due to low electrical resistance and thermodynamic stability.[2] Nanoscale thick TaN is challenging to grow because the nucleation on surface leads to islands in large scale, and the surface is not smooth enough for device fabrication.[3] Etch back process with ALE cycle is one way to reducing the surface roughness.[4] In this work, ALE process for TaN was developed with the following sequential reaction: surface oxidation and removal with fluorocarbon plasmas. In the surface modification step, the TaN surface was oxidized to tantalum oxide (TaO_x) using O_2 plasma. The oxygen atomic concentration was saturated to 31% after 300 second and the thickness change of the converted TaO_x layer was about 1.4 nm. In the removal step, the TaO_x layer was converted to tantalum fluoride (TaF_x) by fluorocarbon plasmas in a temperature range of 25 to 300°C. The etch rate of TaN increased in the temperature range of 25 to 300 °C during the removal step. The etch rate of TaN was self-limited at 1.3 nm/cycle in the time of 120 seconds with a fluorocarbon plasma.

References

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Keywords: Atomic layer etching, Tantalum nitride etching

ALE-SuP-8 New Oxidants for Cu ALE via In Situ XAS Mechanistic Study*, **Adam Hock**, P. Panariti,* Illinois Institute of Technology

Sub-10 nm scaling comes with unprecedented challenges for semiconductor fabrication. Atomic Layer Etching (ALE) is a technique that is becoming increasingly important in semiconductor fabrication, however, it has yet to be widely adopted. Many examples of ALE use harsh chemistry such as halogenated compounds or plasma, which result in damaged and non-conformal structures. Copper is an important interconnect material, so scalable copper ALE is of high importance and further research of both metallic Cu activation and etch are required. Oxidation of metallic Cu surfaces with unselective oxidants (H_2O_2, O_3, oxygen plasma etc.) tend to produce multiple oxidation states of Cu (+1 and +2) as well as Cu mobility at elevated temperatures. This study reports a comparison between conventional oxidants as well as milder, more selective oxidizing agents that produce a more controlled oxidation of Cu surfaces.

X-ray absorption spectroscopy (XAS) was used to directly observe Cu oxidation under oxidation conditions.Temperatures from ambient to 145°C were screened with oxidants and oxidation was found to be to Cu_2O to detection limits.The depth was controllable from less than 2nm to complete oxidation under the conditions studied.The oxidation could be controlled by process conditions and, more importantly, by the nature of the oxidation reagent.These data are compared to *in situ* TEM measurements of Cu particles and measured oxidation thickness as a function of oxidant exposure and found to be comparable.The XAS technique was further benchmarked using conventional XPS measurements.These measurements illustrate that XAS is able to probe surface activation for ALE.In addition, XAS provides metal coordination number, oxidation state, and other mechanistic information about the surface metal state.These measurements combine to provide a better understanding of the relationship between oxidant strength versus depth as a function of various oxidants. These results give insight into the etch-per-cycle as well, Cu surface roughening, and other metrics for the final films.

Atomic Layer Etching
Room Baekeland - Session ALE-MoM2
Thermal and/or Isotropic ALE I

Moderators: Steven M. George, University of Colorado at Boulder, Anil Mane, Argonne National Laboratory

10:45am **ALE-MoM2-1 Photon-Activated Metal Ale**, *X. Yang, B. Coffey,* ***John Ekerdt,*** University of Texas at Austin **INVITED**

Long nucleation delays during area selective ALD of metals can lead to unwanted growth outside the patterned regions.Unwanted nucleation also results when a passivating film begins to breakdown.In the event non-selective nucleation occurs on passivated regions, we describe a low temperature ALE route to etch clusters/islands on the passivated regions faster than the desired film.This low temperature route exploits the general finding by others that metal oxides can be etched by a variety of vapor phase etchants – the issue is controlled oxidation while minimizing damage to adjacent surfaces.We present a low temperature route that involves vacuum ultraviolet (VUV) activation of O_2 to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd and Ru.Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.Pd and Ru can be etched at temperatures ranging from 50 °C – 200 °C by co-exposing the zero-valent metal to 1 Torr of O_2 and VUV photons ($6.5 < h\nu < 11.3$ eV) from a D_2 lamp.Density functional theory and nudged elastic bandcalculations are used to understand the diffusion of oxygen into the metal and the kinetic barriers that limit oxidation to the first and second layers.Metal oxidation proceeds because the flux of atomic oxygen is sufficient to compensate for competing recombinative desorption of molecular oxygen.The oxides of Pd and Ru are etched in an ALE half cycle with 0.50 Torr HCOOH vapor exposure for 30 sec.Metal islands/nuclei are completely oxidized in an exposure cycle while oxidation of a film is limited to approximately one atomic layer.

Photon activation of O_2 in the gas phase above the surface to atomic oxygen leads to an inherently isotropic process since the atomic oxygen can diffuse to any exposed surface before the atomic oxygen is lost through gas-phase loss reactions.This talk will also discuss the use of halogenated hydrocarbons that can possibly adsorb at the process temperature and be activated in the adsorbed state to restrict metal oxidation to those surfaces exposed to the photons.

11:15am **ALE-MoM2-3 Plasma-Assisted Thermal-Cyclic Etching of Silicon Germanium Selective to Germanium**, ***Kazunori Shinoda,*** Hitachi , Japan*; H. Hamamura,* Hitachi, Japan*; K. Maeda, M. Izawa,* Hitachi High-Tech, Japan*; T. Nguyen, K. Ishikawa, M. Hori,* Nagoya University, Japan

Silicon germanium (SiGe) and germanium (Ge) may play an important role in future generations of semiconductor devices. For example, one candidate of future logic devices will be a Ge-channel gate-all-around field-effect transistor (GAA FET), which may require lateral selective etching of the SiGe sacrifice layer with respect to the Ge-channel layer. Isotropic, self-limiting cyclic etching of SiGe selective to Ge will thus be attractive in developing future generations of logic devices. This paper addresses plasma-assisted, thermal-cyclic etching of SiGe, which is selective to Ge. Experiments were conducted with several SiGe and Ge samples with different Ge content. Radical-exposed surfaces of the samples were produced in plasmas excided with hydrofluorocarbon-based gas mixtures that contain nitrogen. Nitrogen was added to the gas mixture because it is essential for forming ammonium-salt-based modified surfaces. Photoelectron-emission measurements were conducted after transferring the samples in vacuum into an x-ray photoelectron spectroscopy (XPS) system under ultra-high vacuum. The XPS spectra obtained after radical exposure consisted of a nitrogen 1s peak at 402 eV, which was likely ascribed to the N-H bond. One explanation of this observation is that a modified surface that consists of ammonium salt formed on the surface of the samples after radical exposure. The intensity of the N-H peak decreased as the Ge composition in the samples increased. The nitrogen 1s peak at 402 eV disappeared when the samples were heated at 100°C. This suggests that the ammonium-salt-based modified surface decomposes and desorbs from the film during heating. We conducted cyclic etching of SiGe and Ge samples with an etching tool developed for 300-mm wafers. Radical exposure and infrared heating were repeated multiple times with this tool. The etching depths of the samples were evaluated using in-situ ellipsometry. The thickness of the SiGe decreased as the number of cycles increased. The etched amount of SiGe in one cycle ranged from 3 to 7 nm. The etched amount of the Ge in one cycle was smaller than that of the SiGe. A maximum SiGe selectivity of 5 was obtained with respect to Ge at optimum stage temperature during radical-exposure steps. The selectivity was due to the selective formation of the ammonium-salt-based modified surface on SiGe compared with that on Ge. The etched amount for one cycle of SiGe and Ge exhibited saturation behavior as the radical-exposure time increased. Self-limiting thermal-cyclic etching of SiGe selective to Ge was thus successfully demonstrated.

11:30am **ALE-MoM2-4 Thermal Atomic Layer Etching of Cobalt with Chlorine Plasma and Hexafluoroacetylacetone (Hhfac)**, ***Yongjae Kim****, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

Copper is widely adopted for interconnect lines in semiconductor devices, but the resistance increases of copper is rapidly increasing due to surface scattering of electrons. [1] Cobalt is considered as an alternative metal because cobalt does not require a barrier/liner and has less resistance than copper below 10nm in dimension. [2] Chemical-mechanical polishing (CMP) processes are used for planarization in interconnect, but they leave interlayer dielectric (ILD) defects due to slurry particles and mechanical forces. Atomic layer etching (ALE) process can be an alternative to reducing the defects in cobalt removal. In this work, ALE process was performed for cobalt in an inductively coupled plasma (ICP) reactor. The ALE process consists of two steps: surface modification with chlorine plasma and ligand volatilization with hexafluoroacetylacetone (Hhfac). In the first step, the surface of cobalt is chlorinated to $CoCl_2$ using chlorine plasma. In the second step, the $CoCl_2$ layer was removed by ligand volatilization with Hhfac. Cobalt ALE process was conducted with changing process temperature at 100~250 degree, and the ALE window was confirmed. Etch rate of cobalt was self-limited at the Hhfac injection time of 90 second. The thickness of the cobalt film before and after the ALE process was confirmed by cross-sectional SEM imaging. The etch rate of cobalt could be controlled below 1 nm/cycle. Surface roughness was compared according to process temperature and chlorine plasma power.

References

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Keywords: Atomic layer etching, Cobalt etching

11:45am **ALE-MoM2-5 Thermal-Cyclic Atomic Layer Etching of Cobalt by Plasma Oxidation and Organometallization**, ***Sumiko Fujisaki,*** Hitachi Ltd,. R&D group, Japan*; Y. Yamaguchi,* Hitachi, Ltd., R&D group, Japan*; H. Kobayashi,* Hitachi High-Tech, Japan*; K. Shinoda, M. Yamada, H. Hamamura,* Hitachi, Ltd., R&D group, Japan*; K. Kawamura, M. Izawa,* Hitachi High-Tech, Japan **INVITED**

The technology node has been scaled down to below 10 nm, and gate-all-around (GAA) FET and C-FET are expected to be utilized in logic devices in the near future.

Isotropic atomic-layer etching (ALE), which can perform atomically precise removal, plays an important role in semiconductor manufacturing under these circumstances. Highly selective ALE is required to process new materials for miniatulized 3D devices. Over the past several years, isotropic ALE of various materials has been reported, including thermal ALE for metal oxides and thermal-cyclic ALE for nitride films [1]. To meet the requirements concerning the variety of materials to be etched, isotropic ALE of cobalt must be developed—for example, for advanced interconnect metallization. Thermal ALE of cobalt by using formic acid and ligands has been reported [2]. Also, the authors have successfully demonstrated isotropic ALE of cobalt film with smoothly etched surfaces by introducing a two-temperature process [3].

The experimental apparatus used in this study is a 300-mm ALE tool equipped with an inductively coupled plasma source and infrared (IR) lamps. One cycle of the thermal-cyclic ALE process is divided into two major steps: oxidation and organometallization. In the first step, the surface of cobalt film is oxidized by oxygen plasma at low temperature, and in the second step, it is converted into an organo-cobalt complex by diketone at high temperature. The organo-cobalt complex then desorbs from the film surface due to its higher volatility. This two-temperature process is crutial because it enables well-controlled etching that leads to a smoothly etched surface. Our ALE tool exhibits a short processing time thanks to its IR lamps for rapid heating. It is desirable that the cobalt oxide formed in the first step be completely removed in the second step (i.e., within one cycle), so the etched amount is controlled by the oxidation thickness of cobalt and the number of cyclic repetitions.

The mechanism of the cobalt ALE reaction was examined by x-ray photoelectron spectroscopy (XPS). Several oxygen 1s peaks were detected in the range of 525 to 535 eV after plasma oxidation at various temperatures. A peak at 530 eV, which preferentially decreased after being exposed to diketone, is the dominant oxidation state for organometallization, and is presumably ascribed to divalent cobalt oxide. It also implies that some other oxidation states of cobalt are removed after converting to the oxide with a 530-eV oxygen 1s XPS peak.

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Atomic Layer Etching
Room Baekeland - Session ALE1-MoA
Thermal and/or Isotropic ALE II

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Adrie Mackus, Eindhoven University, Netherlands

1:30pm **ALE1-MoA-1 Chlorination and Ligand Addition for Thermal ALE of Metals***, **Jessica Murdzek**,* University of Colorado Boulder*; A. Lii-Rosales,* Lam Research Corp*; S. George,* University of Colorado Boulder **INVITED**

Thermal atomic layer etching (ALE) is defined by sequential surface modification and volatile release reactions. Thermal ALE of metals is particularly challenging because the oxidation state of the metal must be changed to match the oxidation state of the volatile metal etch product. After changing the oxidation state, the metal then needs to form a stable and volatile complex. In this work, Ni and Co ALE are developed by oxidizing the metal via chlorination using SO_2Cl_2. Subsequently, the metal is etched by addition of an L ligand to the metal center to create a stable, volatile etch product, MCl_xL_y (Figure 1). The L ligands explored in this work were PMe_3 and tetramethylethylenediamine (TMEDA).

The chlorination and ligand-addition approach for metal ALE is based on the Covalent Bond Classification (CBC) method. X ligands are one-electron donors like Cl and other halogens. L ligands are two-electron donors like PMe_3. TMEDA is a bidentate ligand.One TMEDA ligand acts as two L ligands since TMEDA binds to the metal center through the lone electron pairs on the two nitrogen groups.According to the CBC method, nickel complexes typically have NiX_2L_3 or NiX_2L_2 configurations.Likewise, cobalt complexes are typically found in the CoX_2L_4, CoX_2L_2, or CoX_3L_3 configurations. The goal for Ni or Co ALE is to create these volatile metal compounds using sequential SO_2Cl_2 and L ligand surface reactions.

Both Ni and Co ALE have been studied with in situ quartz crystal microbalance (QCM) and X-ray reflectivity (XRR) to determine etch rate.Quadrupole mass spectrometry (QMS) was also employed to determine the volatile metal-containing etch species. Using SO_2Cl_2 and PMe_3, Ni etch rates varied from 0.1-3 Å/cycle at temperatures from 75-200 °C.QMS measurements also identified $NiCl_2(PMe_3)_2$ (NiX_2L_2) as the stable volatile etch product.Cobalt ALE using SO_2Cl_2 and TMEDA displayed etch rates from 1-12 Å/cycle at temperatures from 175-300 °C (Figure 2). QMS measurements also detected $CoCl_2$(TMEDA) (CoX_2L_2) as the stable volatile etch product.In addition, cobalt can be etched using SO_2Cl_2 and PMe_3 from 70-200 °C, with etch rates between 2-4 Å/cycle. These two Co ALE pathways are complementary with TMEDA useful at higher temperatures and PMe_3 useful at lower temperatures.

Many other X and L ligands could define additional halogenation and ligand-addition reactions.Using the CBC method as a guide, this strategy should lead to the development of various other metal ALE processes.

2:00pm **ALE1-MoA-3 Thermal ALE of Molybdenum via Low Temperature Oxidation in Ozone and Wet Chemical Oxide Dissolution***, **Antoine Pacco**,* IMEC, Belgium*; N. Teppei, S. Iwahata, A. Iwasaki,* SCREEN, Japan*; E. Altamirano Sanchzez,* IMEC, Belgium

Over the last decade, isotropic metal recess has received increased attention due to its relevance for both logic and memory applications. Controllable partial recess of metal requires a high level of accuracy, uniformity, and selectivity. In this work, we present atomic layer etching (ALE) of Mo for its application for Mo recess in buried power rail (BPR) [1] and 3D-NAND structures. Given its improved conductivity at sub 20 nm dimensions, Mo could be a possible candidate to replace W [2].

ALE of Mo thin films was achieved using a sequential oxidation in ozone gas followed by the removal of the molybdenum oxide by simple wet chemical etching. Oxidation in ozone gas has a lower activation energy than in oxygen, thereby effectively reducing the temperature budget of the etching process. We found that the molybdenum oxide formed during oxidation was MoO_3. This Mo (VI) oxide is easier to dissolve in aqueous alkaline solutions than WO_3 which has very low solubility in aqueous solutions [3] and requires more complex removal mechanisms [4-5]. Finally, the underlying Mo metal was unaffected in the aqueous alkaline solutions used allowing for a *selective* removal of MoO_3 as required by an ALE method.

Recess of blanket films as well as patterned samples was studied using this cyclic process and the etch per cycle (EPC) was increased by increasing the oxidation temperature. We were able to tune the EPC between 2 and 6 nm by increasing the substrate temperatures from 180 to 290 °C. No significant differences in EPC were observed between the recess of Mo metal deposited by either plasma vapor deposition (PVD) or atomic layer deposition (ALD). The effect of an annealing step on recess amount was also investigated. Ultimately, roughening of the surface, a typical unwanted effect from conventional *continuous* wet etching of polycrystalline materials [6], was mitigated by this method.

We found that the thermal-wet ALE presented here is capable of recessing Mo isotropically and selectively towards a broad range of materials (Si, SiO_2, SiN, Al_2O_3, ...). Therefore, applications such as next-generation interconnects, BPR and 3D-NAND memory devices could benefit from this cyclic recess etch method.

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2:15pm **ALE1-MoA-4 Selective Thermal Atomic Layer Etching of CoFeB Over MgO by Sequential Exposure to Chlorine and Diketone***, M. Konh, **Andrew V. Teplyakov**,* University of Delaware

Thermal atomic layer etching (ALE) is one of the most promising methods to have precise control of the thin film thickness is required for fabrication of microelectronic devices. CoFeB alloy films are commonly used as ferromagnetic layers in magnetic tunnel junction for integrated memory devices, where they are usually separated by an insulating barrier layer such as MgO. It is important to have a method that can selectively reduce the thickness of CoFeB alloy thin film without affecting MgO layer. Here, selective thermal atomic layer etching of CoFeB alloy thin film using sequential exposure to chlorine and acetylacetone (acacH) is investigated. During the ALE process the concentration of each element in the alloy remains constant according to the X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) is used to indicate the surface morphology preservation after the ALE process. The changes in thickness following thermal ALE on the patterned samples are recorded by AFM to deduce the etch rate, and to evaluate the ALE process on MgO patterns deposited on top of the CoFeB alloy films. To uncover the molecular mechanism of the ALE process, temperature programmed desorption (TPD) experiments are performed to detect possible key desorbing fragments.

2:30pm **ALE1-MoA-5 Ligand-Exchange and Etching Reactions between Metal Fluorides and Silane Precursors Containing Different Ligands***, A. Lii-Rosales, V. Johnson, A. Cavanagh,* University of Colorado Boulder*; A. Fischer, T. Lill,* Lam Research Corporation*; S. Sharma, **Steven George**,* University of Colorado Boulder

Metal fluorides can be spontaneously etched by ligand-exchange reactions. During these reactions, the exchange of ligands between the incoming precursor and the metal fluoride leads to the volatilization of the metal fluoride. These ligand-exchange reactions are important in many thermal atomic layer etching (ALE) processes. To test the effectiveness of different ligands for ligand exchange, the spontaneous etching of metal fluorides by silane precursors containing different ligands was investigated using *in situ* quadrupole mass spectrometry (QMS). The metal fluorides were GaF_3, InF_3, ZnF_2, ZrF_4, HfF_4, and SnF_4. The silane precursors were $SiCl_4$, $SiCl_2(CH_3)_2$, $SiCl(CH_3)_2H$, and $Si(CH_3)_4$. These silane precursors provide Cl, CH_3 or H ligands for the ligand-exchange reaction.

The QMS results showed that F/Cl ligand exchange was observed for all the metal fluorides with the chlorine-containing silane precursors. In addition, all the volatile metal etch products were metal chlorides, namely $GaCl_3$, $InCl_3$, $ZnCl_2$, $ZrCl_4$, $HfCl_4$, and $SnCl_4$. Results for $SiCl_2(CH_3)_2$ on GaF_3 are shown in Figure 1. No metal methyl complexes were detected as volatile metal etch products indicating no F/CH_3 exchange. For $SiCl(CH_3)_2H$ as the silane precursor, the observation of $SiF_2(CH_3)_2$ indicated that F/H exchange is also possible in addition to F/Cl exchange. For the various metal fluorides, the dominance of F/Cl exchange led to nearly equivalent onset temperatures for ligand exchange and for etching to yield metal chlorides as displayed in Figure 2.

Thermochemical calculations of the ligand-exchange reactions verified the formation of metal chlorides. All F/Cl exchanges were thermodynamically favorable as demonstrated by the negative changes in Gibbs free energy (ΔG). These experimental and theoretical results provide guidelines for designing thermal ALE processes. After the fluorination reaction to produce metal fluorides during thermal ALE, ligand-exchange reactions using Cl-containing silane precursors should be effective for etching if the metal fluoride has corresponding volatile and stable metal chlorides.

2:45pm **ALE1-MoA-6 Thermal Atomic Layer Etching of Zinc Sulfide (ZnS) Using Sequential Al(CH_3)$_3$ and HF Exposures***, **Taewook Nam**, J. Partridge, J. Murdzek, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) processes have been developed from many materials including various oxides, nitrides and metals. This study introduces the thermal ALE of a sulfide material - zinc sulfide (ZnS). ZnS thermal ALE was demonstrated using trimethylaluminum ($Al(CH_3)_3$, TMA) and hydrogen fluoride (HF) as the reactants at temperatures from 225 to 300°C. The ALE was performed on ZnS atomic layer deposition (ALD) films that were deposited using diethylzinc ($Zn(C_2H_5)_2$, DEZ) and hydrogen sulfide (H_2S) as the precursors on p-type Si wafers at growth temperatures from 100 to 300°C. The etch rates were determined by monitoring the thickness of the ZnS ALD films using in-situ spectroscopic ellipsometry. Quadruple mass spectroscopy (QMS) was also used to detect the volatile etch products during ZnS thermal ALE to determine the ALE mechanism.

For the ZnS ALD films grown at 100°C, the etch rate varied from 1.4 Å/cycle at 225°C to 2.2 Å/cycle at 300°C. For the ZnS ALD films grown at 300°C, the etch rate was slightly lower and varied from 0.8 Å/cycle at 225 °C to 1.9 Å/cycle at 300°C. The ZnS ALD films grown at 300°C may have slightly higher densities that slow the etch rate. The ZnS ALD films were amorphous according to X-ray diffraction analysis. However, for the ZnS ALD films grown at 300°C, small islands remained on the surface after most of the ZnS ALD film was etched away. After the ZnS thermal ALE, these islands were confirmed as crystalline ZnS particles by XRD.

QMS analysis of the volatile etch products resulting from the sequential $Al(CH_3)_3$ and HF exposures revealed evidence for a conversion mechanism for ZnS thermal ALE as shown in Figure 1. During this conversion mechanism, $Al(CH_3)_3$ converts the top of the ZnS film to an Al_2S_3 surface layer and releases $Zn(CH_3)_2$ as the volatile product. Subsequently, HF fluorinates the Al_2S_3 layer to AlF_3 and releases H_2S as the volatile product. Then $Al(CH_3)_3$ removes the AlF_3 layer by ligand-exchange and also converts more ZnS to Al_2S_3. These reactions release various $AlF(CH_3)_2$ dimers and trimers from ligand-exchange and $Zn(CH_3)_2$ from the conversion. The volatile products measured by QMS during several sequential $Al(CH_3)_3$ and HF exposures are displayed in Figure 2.

3:00pm **ALE1-MoA-7 Requirements Beyond Etch Per Cycle for Thermal ALE in Semiconductor Manufacturing***, **Martin McBriarty**,* EMD Electronics

Isotropic ALE is poised to enter high volume manufacturing (HVM) of semiconductor devices within this decade. Several new process steps enabling more complex logic and memory architectures will incorporate ALE chemistries derived from fundamental research in academic and industrial R&D labs. The rigorous requirements of HVM introduce significant challenges for ALE integration, such as high selectivity, good process control in high aspect ratio features, and extremely low levels of contaminants and residues. Safety and sustainability are also key concerns, as ALE reagents and byproducts are often corrosive, toxic, or have high global warming potential. The choice of candidate chemistries and types of laboratory experiments at the early stages of ALE research can help identify processes which can be more seamlessly integrated into HVM. This presentation aims to clarify some of the semiconductor industry's pressing ALE needs beyond a good etch per cycle, with recommendations for how researchers can strengthen the impact of ALE experiments.

Atomic Layer Etching
Room Baekeland - Session ALE2-MoA

Plasma and/or Anisotropic ALE I

Moderators: Rémi Dussart, GREMI CNRS/Université d'Orléans, Geun Young Yeom, Sungkyunkwan University

4:00pm **ALE2-MoA-11 From Barrel to ALE: A Lifetime in Etch/A Material and System Design Perspective***, **Mike Cooke**,* Oxford Instruments , UK **INVITED**

Plasma etching has accompanied advances in lithography for decades, both necessary to enable higher component density in semiconductor device manufacture. A low-pressure glow discharge can provide both chemically active radicals and directional energetic ion bombardment to a surface, driving chemistry which would otherwise require high temperatures. We will describe the principal formats of plasma etch tool, and their merits for delivering atomic layer etching.

Plasma etching equipment of all formats share some common concerns: avoiding etching the chamber or contaminating the wafer; suppression of unwanted parasitic plasmas; maintaining cleanliness; delivering a uniform process across the substrate and reliably from substrate to substrate; and safe operation. The talk will comment on lessons learned in working with plasma tools for more than 40 years, and on the prospects for evolution of the techniques.

4:30pm **ALE2-MoA-13 Understanding the Self-limiting Behavior in Atomic Layer Etched HfO_2***, **Souvik Kundu**, T. Schram, F. Lazzarino, J. de Marneffe, P. Bezard, S. Decoster, I. Asselberghs,* IMEC, Belgium

For future generation transistor applications, two-dimensional (2D) channel materials have received significant research attention due to their favorable electronic properties. In aggressively scaled devices, selectively removing the top high-k layer from the 2D channel material is not possible by the conventional continuous plasma etching (CE) mainly due to poor etch selectivity between 2D and high-k materials, which leads to unwanted roughness and snap the channel layer below. In this regard, an alternative etching technique is required where the process variability can be controlled precisely, and the preferred layer can be removed using self-limiting reactions without punching through the layer below. The atomic layer etching (ALE) of HfO_2 with BCl_3/Cl_2 radical adsorption followed by low energy Ar+ desorption was investigated to soft-land on its underneath 2D material for Source/Drain *top contacts* formation. Since low ion energies are indispensable to minimize the plasma damage on 2D material, synchronously pulsed (SP) ALE was adopted where the plasma and bias powers were varied synchronously with a 30% duty cycle. The adsorption and desorption times were identified and an ALE window with 0.16 nm etch rate per cycle (EPC), low surface roughness (post-etch), and more than 90% synergy were obtained. Efforts were consecrated to understand the ALE mechanism and the effects of plasma power, bias power, and gas ratio on EPC, and synergy were further studied to understand their roles on ALE window. X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), and atomic force microscope (AFM) were employed to characterize the post-etch HfO_2 surface and interfaces. To realize the efficacy of SP ALE, 10nm HfO_2 was etched from the *10 nm HfO_2/capped seed layer/3mono-layers WS_2/2 µm SiO_2/Si* stacks, where the WS_2 layer is exposed and the signature of non-etched WS_2 layer was confirmed by the results obtained from Raman spectroscopy, XPS, and AFM. In contrast to SP ALE, when a CE process is concerned, it was ascertained that the WS_2 layer is completely ruptured during the HfO_2 etch and eventually lands on the SiO_2 layer below. The challenges of SP ALE and transferring the process on patterned wafers will also be discussed.

4:45pm **ALE2-MoA-14 Area-Selective Atomic Layer Etching of SiO_2 Using Silane Coupling Agent***, A. Osonio, **Takayoshi Tsutsumi**,* Nagoya University, Japan*; B. Mukherjee, R. Borude,* ASM International, Netherlands*; N. Kobayashi, M. Hori,* Nagoya University, Japan

An inherently area-selective atomic layer etching (ALE) process for silicon dioxide (SiO_2) over silicon nitride (SiN) is demonstrated in this study with the use of 1H, 1H, 2H, 2H perfluorooctyltrichlorosilane (POCS), a silane coupling agent. The area-selective adsorption of the chosen silane precursor is leveraged to achieve a substrate-dependent selectivity without the need for surface inhibitors at low substrate temperature (50ºC). A 100 MHz CCP plasma was used for the PE-ALE process. POCS was introduced in gas phase to the vacuum chamber, where the substrate and blanket samples were heated to 50ºC. Low energy Ar^+ bombardment without a bias power followed to remove the modified layer. The changes on the samples' thickness were monitored real-time using *in-situ* spectroscopic ellipsometry (SE) while the changes in the surface functional groups were investigated using *in-situ* FTIR spectroscopy.

Using *in-situ* SE, the area-selective chemisorption of the POCS on SiO_2 over SiN was confirmed from the increase in thickness after dosing which, at the same time, exhibits self-limiting characteristics. *In-situ* FTIR studies confirmed the functionalization of SiO_2 with the CF_2 and CF_3 functional groups and the simultaneous removal of the free OH on the surface during the modification step. After the Ar plasma exposure for the etching step, the removal of the CF_x bonds and the increase in the absorbance of the free -OH peak were found, related to the consumption of the modified layer. Overall, the work shows an alternative course to realize an ideal ALE process that has both self-limiting modification and etching steps. It attempts to address the challenges of stringent parametric control on existing area-selective ALE processes for SiO_2 using other fluorocarbon chemistries.

5:00pm **ALE2-MoA-15 Improving SiO_2 toSiN$_x$ ALE Selectivity with Surface Pre-functionalization for SiO_2/SiN$_x$ Stacks*, Xue Wang,*** Colorado School of MInes*; R. Gasvoda, P. Kumar, E. Hudson,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

The downscaling of semiconductor devices to sub-7nm generation will require increasingly high etching selectivity with atomic-scale control over the etch profiles in high aspect ratio device structures. Plasma-assisted atomic layer etching (ALE) is a promising technique to tackle these challenges. We previously demonstrated that in ALE, selectivity for SiO_2 over SiN$_x$ can be achieved through the selective pre-functionalization of the SiN$_x$ surface with aldehydes prior to etching. Etching was performed using a cyclic C_4F_6/Ar and Ar plasma ALE process. We used *in situ* attenuated total reflection Fourier transform infrared spectroscopy to monitor the changes in the surface chemical composition on SiN$_x$ and SiO_2. Pre-functionalization of a pristine, plasma-deposited SiN$_x$ surface with benzaldehyde accelerated the formation of a graphitic hydrofluorocarbon layer, which in turn lowered the initial loss of SiN$_x$ prior to an etch stop. However, in technological applications, both SiN$_x$ and SiO_2 surfaces are either exposed to atmosphere or are used as stacks where the underlying SiN$_x$ surface is already exposed to an etching plasma before it can be dosed with the hydrocarbon (see Fig.1a). An atmosphere-exposed SiN$_x$ surface forms a skin layer of SiO_xN_y, and an SiN$_x$ surface exposed to an etching plasma has a layer of residual CF$_x$. In each case, we discovered that the surface –NH$_x$ groups present after plasma deposition are partially to largely removed. While benzaldehyde does not react with SiO_xN_y and SiO_2 surfaces, it readily reacts with the CF$_x$ reside on the plasma etched SiN$_x$ and SiO_2 surfaces, which prevents selective reaction of aldehydes with the SiN$_x$ surface.

In this presentation, we will also show that on partially etched SiN$_x$ and SiO_2 surfaces, benzaldehyde can be attached selectively to the SiN$_x$ surface after one ALE cycle by minimizing the CF$_x$ residue on the SiO_2 surface. Thus, on the SiN$_x$ surface, we utilize the reactivity of the surface –NH$_x$ groups and the residual CF$_x$ layer to obtain selectivity for reaction to benzaldehyde (see Fig.1b). Our results also show that the selectivity of benzaldehyde attachment reduced with the slow accumulation of carbon-rich residue on both surfaces during ALE process. For SiN$_x$ and SiO_2 surfaces that were pre-etched for one ALE cycle, using 4-wavelength *in situ* ellipsometry, we show that benzaldehyde dosing reduced the amount of SiN$_x$ etched and increased the etch selectivity from 1.7 to 2.1 for 20 ALE cycles (see Figure 2). If we introduced a second dose for benzaldehyde after the 5th ALE cycle, which is prior to significant CF$_x$ accumulation on SiO_2, the selectivity could be further improved from 2.1 to 3.4.

5:15pm **ALE2-MoA-16 Plasma-Assisted Atomic Layer Etching of Silicon Nitride with Unfragmented Fluorocarbons*, Chon Hei Lam,*** *M. Carruth,* University of Texas at Austin*; Z. Chen, J. Blakeney, P. Ventzek, S. Sridhar, A. Ranjan,* Tokyo Electron America Inc.,*; J. Ekerdt,* University of Texas at Austin

The self-limiting behavior in atomic layer etching (ALE) processes promise to deliver atomic scale fidelity for three-dimensional device fabrication. ALE processes typically alternate cycles of chemical modification to weaken the surface bonds followed by ion bombardment to remove material with limited amount. ALE may provide fine control over the etch rate and can limit physical damage to the substrate through the layer-by-layer etch process. Since silicon nitride films are a component used in self-aligned multiple patterning schemes, ALE of silicon nitride is an important consideration in process development. ALE using plasma fragmented fluorocarbons can result in undesirable film growth. Ideally, the process should restrict fluorocarbon film build up to avoid taper profiling, clogging or etch stop. We explore ALE of silicon nitride by utilizing undissociated fluorocarbon (CF_4 and CHF_3) adsorption followed by gentle argon ion bombardment. The impact of gas precursors, energetic ion, temperature, and the nature of the surface chemical modification are discussed. We follow the surface chemistry and monitor structural damage during ALE.

Using CHF_3 we illustrate fluorocarbon surface modification and using energetic argon ion bombardment we illustrate changes to the adsorbed layer during bombardment. The ALE steps are performed at 24 °C and 100 °C (Figure 1). The films are characterized by *in situ* using X-ray photoelectron spectroscopy and spectral ellipsometry. The silicon nitride film is exposed to CHF_3 at 30 mTorr for 1 min as the fluorocarbon adsorption step followed by an argon ion bombardment. The F 1*s* peak appears after the (3 min, 100 eV) argon ion bombardment at 24 °C. The energetic argon ions fragment the fluorocarbon and activate the interaction between fluorine and silicon, and lead to the formation of SiF$_x$ (Fig 2a). When the sample temperature is elevated to 100 °C, the SiF$_x$ shoulder appears in the Si 2*p* spectra upon the CHF_3 adsorption step (Fig 2b) demonstrating the reaction between CHF_3 and silicon nitride is thermally activated. An SiF$_x$ feature remains in the Si 2*p* spectra after the ion bombardment. The shoulder from SiF$_x$ is more intense at 100 °C compared to the 24 °C. The ellipsometry result (Fig 1) shows a gradual change of etch rate over the first 5 ALE cycles as the starting surface is partially oxidized and transitions to silicon nitride. After the removal of the oxidized layer, the etch rate increases and corresponds to approximately 1 nm/cycle. The F 1*s* peak intensity remains at the same level after 5 and 10 ALE cycles indicating the residual fluorine on the surface after ion bombardment.

5:30pm **ALE2-MoA-17 Silicon Atomic Layer Etching with Surface Chlorination and Removal with Ar or He Plasma*, Namgun Kim,*** Sungkyunkwan University, Korea (Republic of)*; D. Shin, J. Kim, C. Lee, K. Yoon,* Samsung Electronics, Korea (Republic of)*; Y. Kim, H. Chae,* Sungkyunkwan University, Korea (Republic of)

Si atomic layer etching (ALE) has attracted a lot of attention in the semiconductor manufacturing industry due to its excellent depth uniformity with precise control and damage-less compared to conventional reactive ion etching (RIE). [1] Si ALE is generally consisted of two steps, Cl2 adsorption and Ar desorption. The desorption step is the key process of transferring energy to the modified surface and is a major step that determines selectivity and uniformity. [2] Ar was mainly used as the sputtering gas for the desorption step, and there were few studies on other inert gases. In previous papers, the ALE window range was enlarged and the etch per cycle (EPC) was lowered when He was used as sputtering gas instead of Ar, but the recent GaN He ALE study showed different results. [3][4] In this work, Cl2 based Si ALE process was performed using He or Ar as sputtering gas in an 300mm inductively coupled plasma (ICP) reactor. The range of the ALE window did not change to 25V in either condition, the EPC increased from 5.96 Å/cycle to 7.02 Å/cycle, and a nonself-limited behavior was observed when He was used as the sputtering gas instead of Ar. The oxygen atomic fraction was increased in He ALE compared to Ar ALE when an x-ray photoelectron spectroscope (XPS) was observed by changing the number of cycles and bias power. Both ALE processes were compared with conventional RIE by measuring selectivity and roughness. In conclusion, Si quasi-ALE was successfully performed using Ar or He as sputtering gas with Cl2 plasma in the conventional plasma etching tool, and the difference in ALE performance according to the sputtering gas was also investigated.

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Atomic Layer Etching
Room Baekeland - Session ALE-TuM2

Atomic Layer Cleaning (ALC), ALE Integrated with ALD, and Alternative ALE Approaches

Moderators: Jessica Murdzek, University of Colorado Boulder, Fred Roozeboom, University of Twente & LionVolt B.V., Netherlands

10:45am **ALE-TuM2-1 ALE from Selective Etching to Selective Deposition***, **Christophe Vallee**,* SUNY POLY, Albany*; M. Bonvalot, M. Jaffal,* LTM-CNRS, University Grenoble Alpes, France*; C. Mannequin,* Tsukuba University, Japan*; R. Gassilloud, N. Posseme, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France **INVITED**

Atomic layer etching (ALE) is a powerful process to perform either isotropic or anisotropic etching at the atomic scale with a quasi-infinite selectivity. In this presentation, we will address an emerging technological concept based on the selective etch characteristics of ALE to selectively deposit a material on a patterned substrate on a given surface or space direction. This concept relies on a standard atomic scale deposition process (ALD) sequentially combined with ALE to advantageously lead to a selective deposition process [1-2]. We will show, by discussing examples from the literature, that combining atomic-scale deposition and etching processes offers new perspectives in materials thin film elaboration with accurate control of their physical properties, such as roughness, density and microstructure. We will also discuss various strategies for the optimization of this sequential selective deposition process to overcome its inherent weaknesses in terms of contamination and throughput, in view of its potential implementation in high volume manufacturing lines.

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[2] M. F. J. Vos, S. N. Chopra, J. G. Ekerdt, S. Agarwal, W. M. M. Kessels and A. J. M. Mackus, *J. Vac. Sci. Technol. A***39 (**2021) 032412.f

11:15am **ALE-TuM2-3 Surface Modification for Atomic Layer Etching of TiAlC Using Floating Wire-Assisted Liquid Vapor Plasma at Medium Pressure***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; K. Shinoda, H. Hamamura,* Hitachi, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech, Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Isotropic and selective etching of metal gate materials such as TiC, TiAlC, and TiN is required in the fabrication of fin-type or nanosheet field effect transistor (FET) of logic semiconductor devices. Ternary material TiAlC belongs to high-melting point, high-hardness, and high-wear resistance materials, and there are only few reports for wet etching this material by H_2O_2 mixtures with poor etching performance and device damages. No dry etching of TiAlC has been reported yet. Therefore, development of a high-performance etching method with highly selective and isotropic removal of TiAlC over TiN at an atomic layer level is strongly demanded.

In this study, an atomic layer etching of the ternary material TiAlC has been first developed by a transferring approach from wet etching to dry etching using a floating wire (FW)-assisted liquid vapor plasma of Ar gas mixed with NH_4OH-based liquid vapors. The FW-assisted non-halogen liquid vapor plasma generated at medium pressure can produce a large amount of etchant or co-reactant species to enhance the reaction rate with sample surface. This radical-rich environment (electron density of 10^{14} cm^{-3}) plays a key role in controlling isotropic etching of 3D multilayer semiconductor devices. Surface modifications, such as oxygenation, hydroxylation, hydrogenation, and nitridation of the TiAlC film were obtained by controlling the active radicals, such as O, OH, H, and NH. This leads to form volatile products having chemical bonds including methyl ($Al–CH_3$), methylamine ($Ti–(NH_n(CH_3)_{2-n})$), and alkoxy ($Ti–(OC_nH_{2n+1})$) groups. Thus, the treated TiAlC surface can be removed via the formation of modified layers. A mechanism for selective etching of TiAlC over TiN is proposed here. This FW-assisted plasma technique is expected to be available for highly selective and isotropic atomic layer etching of metal and metal compounds in semiconductor device fabrication.

11:30am **ALE-TuM2-4 Atomic Layer Processing Approach for Achieving Abrupt Epitaxial Interfaces on AlN***, **Virginia Wheeler**, D. Boris, A. Lang, G. Jernigan, N. Nepal, S. Walton,* Naval Research Laboratory

Next generation devices will require novel heterojunctions with abrupt, pristine, defect-free interfaces. Naturally occurring surface oxides on semiconductor materials represent a significant impediment to achieving such interfaces. AlN is one of several ultra-wide bandgap semiconductor of interest for future high power, high frequency devices. Since Al has a high affinity for oxygen, it is hard to completely remove oxygen from AlN surfaces by traditional wet or dry etching methods. Even if successful, AlN immediately reoxidizes during transfer to deposition chambers. This amorphous native oxide layer (typically 3-10nm thick) consists of species with high bond energies requiring temperatures in excess of 900°C to remove, which can alter the characteristics and prevent the formation of an intimate, crystalline optical or electrical interface. Thus, for promoting atomic layer epitaxy at ≤ 500°C a new approach is necessary to attain pristine AlN surfaces.

Here, we merge a low temperature fluorine-based plasma etch process [1] with a etch/passivation technique previously applied to Al mirrors [2], to simultaneously remove the AlN native oxide and passivate the surface with a stable oxi-fluorine film. The process employs a pulsed, electron beam driven plasma produced in an Ar/SF_6 background with an RF substrate bias of -40V. XPS and TEM results show this produced a 1nm $Al_xO_yF_z$ layer that was stable even after 3 days in atmospheric conditions. Temperature dependent XPS revealed that the majority of this layer was removed at 500°C in ultra-high vacuum conditions. AFM and TEM measurements also revealed that the plasma-processed surfaces were slightly smoother than as-received AlN substrates.

To demonstrate the feasibility of this approach as an ex situ process, plasma treated AlN substrates were transferred to a Veeco Fiji G2 ALD system. Samples were exposed to an in-situ anneal at 400°C in 10^{-7} Torr, after which they were cooled under vacuum to 295°C and a 20nm optimum TiN film was deposited. TEM analysis shows a defective, abrupt, interface between the polycrystalline TiN and AlN substrate. EELS was used to show that the majority of the interface has a N-K edge that shifts from AlN to TiN in only 1-2 pixels without any evidence of residual fluorine or oxygen. Occasionally, pyramidal defects containing fluorine and oxygen were observed and resulted in localized crystallinity loss within the TiN film. This demonstrates the importance of clean, abrupt interfaces for promoting epitaxial films by ALD.

[1] S.G. Walton, et al. *J.Vac. Sci. Technol. A***39**, 033002 (2021)

[2] L.V. Rodriguez de Marcos, et al. *Opt. Mat. Expr.***11(3)**, 740-756 (2021).

Atomic Layer Etching
Room Baekeland - Session ALE1-TuA

In situ Studies, Mechanisms and Modeling of ALE

Moderators: Sumit Agarwal, Colorado School of Mines, Dmitry Suyatin, Lund University

1:30pm **ALE1-TuA-1 Surface Reaction Mechanisms by Metal-Organic Compound Formations in Atomic Layer Etching Processes***, **Tomoko Ito,*** Osaka University, Japan*; A. Basher,* King Abdullah University of Science and Technology, Saudi Arabia*; K. Karahashi, S. Hamaguchi,* Osaka University, Japan **INVITED**

Transition metals are known as hard-to-etch materials for reactive ion etching (RIE). In recent years, atomic layer etching (ALE) based on the formation of highly volatile metal compounds from surface metals and organic gases has been proposed as atomically controlled and damage-less etching for transition metals [1]. In chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes, various volatile metal-organic compounds such as β-diketonates (such as nickel(II) acetylacetonate: Ni(acac)$_2$ and Nickel(II) hexafluoroacetylacetonate: Ni(hfac)$_2$) and metallocenes (such as nickelocene) are known as metal precursors. The metal ALE process mentioned above, where volatile metal β-ketone enolates or metallocenes are formed on a metal surface, may be considered as a reverse process of such ALD. The development of new ALE processes for various transition metals requires a better understanding of surface reactions of metals with gas-phase organic molecules. Therefore, the goals of this study are to understand how organic compounds absorb on transition metal surfaces and react with transition metal surfaces. Moreover, we want to clarify the mechanisms of the formation of volatile metal compounds and their desorption processes. In this study, we focused on the surface reactions of Ni and Co with hexafluoroacetylacetone (hfacH) and acetylacetone (acacH) gases, which were analyzed experimentally with the Atomic Layer Process (ALP) Analysis System and theoretically with density functional theory (DFT) calculations [2,3]. The ALP Analysis System, which consists of an *in situ* high-resolution X-ray Photoelectron Spectroscopy (XPS) system and an ALP reaction chamber, allowed us to examine the chemical compositions and bond formation of the metal and metal oxide surfaces on which hfacH or acacH molecules adsorbed. ALE processes of Ni and Co films were also confirmed experimentally with oxidation and hfacH exposure at elevated temperatures. DFT calculationsalso clarified the mechanisms of self-limiting reactions in thermal ALE of Ni with hfacH and acacH exposure, which were found to be consistent with experimental observations.

[1] J. Zhao, et. al., Appl. Surf. Sci. 455, 438 (2018).

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2:00pm **ALE1-TuA-3 Atomic Layer Etching of Al_2O_3 on Metallic Substrates Using *in situ* Auger Electron Spectroscopy***, **Andrew Cavanagh,** S. George,* University of Colorado at Boulder

Ultra-sensitive techniques are required to observe the final cycles of atomic layer etching (ALE) as the etch process becomes a surface cleaning procedure at the interface of the film and the substrate/etch stop. With a sensitivity of ~1% of a monolayer, Auger electron spectroscopy (AES) is well suited for measuring the removal of a film with ALE. AES peak height ratios of the film and the underlying substrate provide a quantitative measurement of the film thickness during ALE. The peak height ratios were evaluated using a model developed by Holloway.

ALE of Al_2O_3 was performed using hydrofluoric acid (HF, 10% solution in pyridine) and trimethylaluminum (TMA). The sample stack was Al_2O_3/Au/Y_2O_3 (adhesion layer) /SiO_2 (native oxide)/Si. The gold underlayer provided a chemically inert, highly conductive interface ideal for AES studies. AES measurements were conducted periodically throughout the etch process and used to determine the thickness of the Al_2O_3 film. The instrument used for these measurements allowed for the transfer of the sample from an ALE process chamber (~1 Torr) to the ultra-high vacuum analysis chamber used for AES (10^{-10} Torr) without exposure to atmosphere.

The reduction in the aluminum and oxygen AES peak intensities from the Al_2O_3 film and the increase in the gold substrate peak intensity was observed as a function of the number of ALE cycles at 250°C (Figure 1). As monitored by AES, the etch per cycle of Al_2O_3 with HF and TMA at 250 °C was determined to be 0.3 Å·cycle^{-1}. At the Al_2O_3 – Au interface, once the Al_2O_3 film had been nominally removed, Al and O atoms remained on the surface. Additional cycles of HF and TMA continued to remove this material, effectively cleaning the substrate surface (Figure 2). AES observations for the Al_2O_3 ALE process on Au substrates will be presented for different reaction conditions.

2:15pm **ALE1-TuA-4 In-situ Optical Emission Spectroscopy as a Tool to Characterize Cyclic Quasi-Atomic Layer Etching***, **Yoana Ilarionova,*** Lund University, Sweden*; M. Karimi,* AlixLabs, Sweden*; D. Lishan, D. Geerpuram,* Plasma-Therm LLC*; R. Jafari Jam, D. Suyatin, J. Sundqvist,* AlixLabs, Sweden*; I. Maximov,* Lund University, Sweden

Atomic layer etching (ALE) is one of the most advanced etching processes today, which enables atomic precision in a cyclic etching, where the material is removed layer-by-layer. In an implementation of ALE, a monolayer of reactive gas is chemisorbed on the surface of the etched material providing surface activation. The activated surface is then removed by plasma - usually by low-energy ions extracted from the discharge. They provide sufficient energy to remove only the reaction products leaving inactivated material.

In practice the ions may contribute to the physical sputtering of the etched material, thus increasing the total etch rate above the values of pure ALE. The residual reactive gas in the reaction chamber can dissociate in the plasma and also increase the etch rate. This etching mode can be defined as a “quasi-ALE” with contributions from the sputtering and reactive ion etching (RIE). To realize a “real or pure” ALE regime with negligibly small unwanted effects, careful optimization of process conditions is necessary. In the current work, we apply optical emission spectroscopy (OES) in a quasi-ALE cyclic process to monitor the relative concentration of active Cl_2 species in the chamber and relate it to the observed etch rate of Si.

In our experiments, we used a commercially available Inductively Coupled Plasma RIE Takachi™ tool (Plasma-Therm LLC, USA) with Cl_2 and Ar as process gases. Silicon samples were patterned with Talbot displacement lithography to produce specimens with resist masks. The etch rates were measured after the samples were cleaved and inspected with a scanning electron microscope. The OES measurements were performed in the wavelength range 191 - 887 nm using an in-situ spectrometer. The etch cycle included the following steps: injection of molecular Cl_2, purging with Ar to remove the excess chlorine, Ar-plasma etching and purging again.

Here we present a correlation between the average Si etch rate per cycle (EPC, determined by the etch depth divided by the number of cycles) and the intensity of the 257 nm Cl-peak as measured by the OES. The peak is generated during the Ar plasma step due to the presence of excess Cl_2. The experiments show that both the EPC and the Cl-peak increase with the increase of injection time and follow the same trend. A dependence between the EPC and the OES intensity is also observed. The measured EPC of 6.3-8.2 Å exceeds the expected EPC for pure ALE, indicating an excess of Cl_2. This indicates that the purging time affects the amount of residual Cl_2. Finally, we also discuss other applications of OES in the optimization of a quasi-ALE process.

2:30pm **ALE1-TuA-5 Atomic Layer Etching of CAR/SOG in EUV Patterning of 300 Mm Wafers - Selectivity and Roughness Mechanisms***, **Francois Loyer**, P. Bezard, R. Blanc, F. Lazzarino, S. De Gendt,* IMEC, Belgium

Future technological nodes (N3 and below) will see further shrinking of not only the pattern dimensions, but of photoresist film-thickness as well. The etching of Spin-On-Glass (SOG) using a Chemically-amplified-resist (CAR) mask following lithography is strongly affected by this trend as the selectivity of the conventional etch processes will soon no longer be sufficient. Furthermore, roughness reduction techniques as we know them will also be challenged as they typically consume some of the already-meagre CAR budget. Therefore, the reactive-ion-etching – based atomic layer etching (RIE-ALE) of SOG with a CAR mask is investigated as a softer and more selective alternative to conventional RIE. The RIE-ALE of SOG and the transfer into underlying hard mask have been demonstrated on coupons as well as on 300 mm full wafers, highlighting a strong increase of selectivity compared to RIE in coupons. However, the ALE process also yielded a higher roughness than RIE which doesn’t meet the requirements for EUV patterning.

An investigation of the mechanisms leading to this improvement of selectivity together with the deterioration of the roughness is provided, highlighting the lack of chemical contrast due to the reactivity of the fluorocarbons, the role of redeposition mechanisms and the importance of interfacial interactions. Indeed, the mechanisms of fluorination during the patterning process become essential to understand and optimize the processes, as the very thin layers become deeply modified within their bulk.

The selectivity observed on patterned wafers can be explained by redeposition mechanisms, as the fluorocarbon-mixed layers formed in ALE are sputtered and redeposit on the CAR mask. Redeposition mechanisms are not suitable for an optimal roughness control as their statistical distribution leads to an increase of the LER and LWR. Moreover, the surface properties of both the CAR photoresist and SOG underlayer being deeply altered during the fluorination, the formation of complex interfaces as the ALE process occurs are expected to occur which induce further stress – hence roughness – within the layers. Surface free energy (SFE) measurements highlight the evolution of the dispersive (*i.e.*, London force) and polar (*i.e.*, Coulomb force) components of the layers during the patterning. Those interactions driving the gas to solid interactions before the formation of the mixed layer and the interface with the bulk, they provide valuable information on the potential stress within the stack.

2:45pm **ALE1-TuA-6 Ab Initio Calculations on the Thermal Atomic Layer Etching of Copper*, Xiao Hu*,** *J. Schuster,* Chemnitz University of Technology, Fraunhofer Institute for Electronic Nano Systems, Center for Materials, Architectures and Integration of Nanomembranes (MAIN), Research Fab Microelectronics Germany., Germany

Copper interconnects are widely used in ULSI circuits due to their low resistivity and superior resistance to electromigration. Traditionally, the patterning of copper and barrier metals in the damascene process relies on chemical mechanical planarization (CMP), which may cause damages to fragile low-k interlayer dielectrics. Thermal atomic layer etching (ALE) is an emerging technique that uses sequential, self-limiting reactions to remove materials with high selectivity [1]. Thermal ALE is being considered an alternative to CMP as a final material removal step in the copper damascene process [2]. Recently, the thermal ALE of copper was demonstrated using O_2 or O_3 and H(hfac) (hexafluoroacetylacetonate) as the reactants [3]. Besides the oxidation mechanism, metal ALE can also be achieved through halogenation and ligand volatilization. For example, Co ALE has been demonstrated using Cl_2 and H(hfac) as the reactants [4]. In this work, theoretical calculations based on density functional theory (DFT) were performed to explore the possibility of Cu ALE through halogenation and ligand volatilization.

Using ab initio thermodynamic calculations, we have compared the Gibbs free energies of the reactions between H(hfac) and CuO, Cu_2O, and $CuCl_2$, as shown in Figure 1. It is found that the CuO + H(hfac) and Cu_2O + H(hfac) reactions are exothermic and have negative ΔG values between 300 K and 700 K. In contrast, the $CuCl_2$ + H(hfac) reactions are only favorable at temperatures higher than 425 K. Thermodynamic calculations suggest that a higher reaction temperature is required for Cu ALE using Cl_2 and H(hfac) as the reactants. In the next, we performed DFT calculations to investigate the elementary reaction steps of Cu ALE. During the Cl_2 exposure, the Cu surface is chlorinated to $CuCl_2$. During the H(hfac) exposure, the surface $CuCl_2$ is converted to gaseous HCl and $Cu(hfac)_2$. The surface reaction between $CuCl_2$ and H(hfac) consists of several elementary steps including H(acac) dissociation, hydrogen diffusion, $Cu(hfac)_2$ formation, and HCl and $Cu(hfac)_2$ desorption. The rate-limiting step is found to be the desorption of HCl and $Cu(hfac)_2$, with an activation energy of about 1.7 eV. Lastly, we focused on the computational evaluation of ligands for $CuCl_2$ volatilization. Various candidate ligands including acac, NacNac, dki, pyrim, dmap, and amd have been considered in this work.

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3:00pm **ALE1-TuA-7 Transport and Reaction Kinetics Modelling of Thermal ALE in High Aspect Ratio Hafnium Oxide Structures*, Andreas Fischer,*** *D. Mui, A. Routzahn, R. Gasvoda, J. Sims, T. Lill,* Lam Research Corporation

Thermal atomic layer etching is rapidly becoming an important complementary processing technology in manufacturing 5 and 3 nm devices in the semiconductor industry.Critically, stacked chip architectures such as 3D NAND and 3D DRAM require conformal isotropic etching to remove material such as HfO_2 in hard-to-reach locations with aspect ratios that can be >50.To achieve repeatable device performance throughout a 3D stack, the removal rate (etch per cycle) of the etched material during an etch process need to be controlled such that the overall etch is the same from top to bottom of the device stack.In this work, we have modelled the reaction kinetics and transport processes of reactants and by-products during a cyclical ligand exchange-based ALE process. This ALE process consists of two steps: a fluorination step, followed by a fluorine-to-chlorine ligand exchange-based removal step.Experimental data revealed that the fluorine dosing during the fluorination step was predominantly responsible for controlling the etch rate of the ALE process but had only a minimal impact on the etch profile inside these holes.The ligand exchange dosing, on the other hand, predominantly controlled the etch profile (depth loading) with equal etch rates top-to-bottom obtained when the step was operated close to saturation.Our model predicts, in agreement with the experiment, that adsorption and reaction rates during fluorination on HfO_2 surfaces are significantly slower than transport times inside these deep holes leading to essentially flat fluorination profiles even if the fluorination step is not operated in saturation mode.In contrast, transport rates with the ligand exchange molecule are slow in comparison but adsorption and ligand exchange rates with the fluorinated hafnium appear to be significantly higher than for fluorine during the fluorination step.Slow transport in combination with high surface reaction rates for the ligand exchange step led to an etch rate that was dependent on aspect ratio (feature depth) in processes that used sub–saturation exposures.

3:15pm **ALE1-TuA-8 Damage Formation in the Underlying Silicon after the Removal of Silicon Nitride by Atomic Layer Etching: A Molecular Dynamics Study*, Jomar Tercero,*** Osaka University, Japan*; A. Hirata,* Sony Semiconductor Solutions Corporation, Japan*; M. Isobe, K. Karahashi,* Osaka University, Japan*; M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; S. Hamaguchi,* Osaka University, Japan

Molecular dynamics simulations were performed for a better understanding of the formation mechanisms and extent of damage in the underlying silicon (Si) material when a silicon nitride (Si_3N_4) layer above it was removed by atomic layer etching (ALE). ALE is an etching technique known to remove a surface layer of a material with atomic-level control and precision. On account of this, extensive research was focused on devising ways to obtain a uniform and stable etching performance with good selectivity to other materials, to cope with high demand from the semiconductor industry. However, though ALE is known to etch a very thin layer at a time, problems such as over-etching or damage on the underlying material layer might still occur during the fabrication [1]. Therefore, in this study, ALE of Si_3N_4 formed on a Si surface was examined, with the use of molecular dynamics simulation. As in experiments, the surface modification step was performed with the adsorption of CH_2F radicals, and the removal step was performed with the irradiation of the modified layer with Ar ions. To assist the removal of the remaining HFC species, O ions were introduced after the removal step. Recent experimental observations showed that the HFC species penetrated deeply into the underlying Si during the first ALE cycle [2]. Our simulation showed that the HFC and Si_3N_4 species penetrated the underlying Si material to a depth of around 4 nm, in the removal step with 300 eV of Ar ion incident energy. The higher the Ar ion incident energy was, the deeper penetration depths of the HFC were observed. Moreover, the bond distributions showed that those penetrated species formed chemical bonding with surrounding Si atoms. As a consequence, the extent of damage or the thickness of the amorphized Si layer was also found to be around 4 nm. The results also showed that physical sputtering tended to dominate the ALE process as the Ar ion incident energy increased, where a large number of monoatomic species left the surface during the removal step. The results suggest that the Ar ion incident energy has a significant contribution to the damage generation in the underlying Si material.

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Atomic Layer Etching
Room Baekeland - Session ALE2-TuA

Plasma and/or Anisotropic ALE II

Moderators: Ankur Agarwal, KLA-Tencor, Christophe Vallee, SUNY POLY, Albany

4:00pm **ALE2-TuA-11 Plasma Processes for Isotropic and Anisotropic Atomic Layer Etching*, Adrie Mackus,*** Eindhoven University of Technology, Netherlands **INVITED**

While plasma etching has been the cornerstone technology in semiconductor fabrication in the past decades, future technology nodes require material removal with atomic-level accuracy as provided by atomic layer etching (ALE). Plasmas conventionally allow for anisotropic etching with high etch rates because synergistic effects between ions and radicals accelerate the surface reactions. In anisotropic ALE, more accurate control is obtained by decoupling the ion and radical contributions. Radical-dominated plasmas can also be employed for isotropic ALE, an option that is largely unexplored compared to the recent focus on thermal chemistries. In this contribution, plasma processes for both isotropic and anisotropic ALE are discussed, focusing on the unique merits provided by plasmas when accurately tuning the exposure to specific plasma species.

For isotropic ALE, two different types of chemistries were explored: (1) surface fluorination by SF$_6$ plasma exposure, followed by ligand-exchange reactions,[1] (2) diketone etchant (e.g. Hhfac, Hacac) exposure, followed by a plasma clean step.[2] The main merits of using plasmas for isotropic etching as compared to thermal chemistries were demonstrated for the fluorination / ligand-exchange process, namely the ability to etch at lower temperatures and with a higher etch per cycle. For the second process, in-situ Fourier transform infrared spectroscopy studies reveal that the self-limitation of the diketone etching reaction relies on the adsorption of diketone species in bonding configurations that do not contribute to etching. The ability of plasmas to effectively remove deactivating species and restore the original surface enables new ALE chemistries.

Although the ion energy is the most important parameter in anisotropic ALE, conventional radio-frequency biasing typically provides a broad distribution of ion energies. Ions with a well-defined energy are obtained in our work by employing tailored waveform biasing.[3] This precise control of the ion energy allows for sputtering in between the thresholds of chemically-modified and bulk materials, thereby opening up ion energy windows for highly-synergetic or -selective etching.

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4:30pm **ALE2-TuA-13 SF$_6$ and Ar Plasma Based Atomic Layer Etching of Gallium Nitride (GaN)***, **Lamiae Hamraoui**, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; M. Boufnichel,* STMicroelectronics Tours, France*; R. Dussart,* gremi CNRS/Université d'Orléans, France

Gallium nitride (GaN) is a powerful and promising semiconductor that perfectly fills and enhances the function obtained with silicon in technology development and in the fabrication of next generation of high-power devices as for example, the normally-off High Electron Mobility Transistors (HEMTs). The development and optimization of a damage-free etching process is still a research topic. Therefore, the Atomic Layer Etching (ALE) process has become predominant for the development of GaN-based HEMT and the conservation of its electric characteristics since it provides more precise etching depth and is less damaging compared to continuous plasma etching.

Up to today, the largest part of the research on the GaN ALE process has been carried outusing chlorine-based chemistries for the modification step, considering that the GaCl$_3$ etch by-product is volatile under ion bombardment [1,2]. However, the fluorinated chemistry is less investigated as compared to the chlorinated chemistry for the ALE of GaN [3,4]. This is primarily due to the non-volatility of GaF$_x$ etch by-products as the GaF$_3$, which has a boiling temperature of 1000°C at atmospheric pressure [5]. Among the few fluorine based GaN ALE research reports, K. Nakazawa et al [3] have performed a two-step ALE process that involves a CF$_4$/O$_2$/Ar plasma adsorption step and an Ar plasma with ion bombardment activation step. A separate study of thermal ALE of GaN using fluorine chemistry was carried out by another group where each cycle is initiated by an exposure to XeF$_2$ gas, followed by an Ar purge step, and lastly an exposure to BCl$_3$ gas [4].

In our work, the ALE of GaN process consists of a cyclic modification (fluorination) step using SF$_6$ plasma and an Ar plasma removal step performed in an Inductively Coupled Plasma (ICP) reactor. In this paper we report on the results of energy scan, the synergy and the self-limiting regime of ALE process using fluorinated chemistry. The influence of different plasma parameters such as the ICP power and the pressure on the Etch Per Cycle (EPC) and the RMS surface roughness was also investigated using Atomic Force Microscopy.

The authors would like to thank the European Union (IPCEI standing for Important Project of Commun European Interest) and Région Centre Val de Loire for their support through the Nano2022 project. We also acknowledge CERTeM 2020 platform, which has provided the majority of the equipment.

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4:45pm **ALE2-TuA-14 SF$_6$ Physisorption based Cryo-ALE of Silicon***, **Jack Nos**, G. Antoun, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; A. Girard, C. Cardinaud,* IMN CNRS/Université de Nantes, France*; R. Dussart,* GREMI CNRS/Université d'Orléans, France

Cryogenic Atomic Layer Etching (Cryo-ALE) using C$_4$F$_8$ as a precursor gas has been previously presented as an alternative method to achieve ALE of SiO$_2$. In this process, C$_4$F$_8$ is injected in gas phase during the "chemical modification" step, in order to physisorb on a cooled SiO$_2$ surface. The etching step is then achieved using an Ar plasma with a low energy ion bombardment. The temperature window of this process was between -120°C and -90°C [1,2]. A self-limiting etching regime was obtained with a regular etch per cycle (EPC) through several tens of nanometers which demonstrates the process stability without any contamination of the reactor walls.

In this paper, we show the results using SF$_6$ molecules as precursors for cryo-ALE of silicon.

In 1996, Royer *et al.* studied the chemisorption of sulfur and fluorine on Si during a simultaneous exposure to SF$_6$ gas and Ne$^+$ ion beam. In this work, they showed by XPS measurements that the fluorine quantity on the Si surface tends to increase as the temperature decreases, for a process window between 20°C and 130°C [3]. Therefore, a cryo-ALE study based on SF$_6$ physisorption was carried out to extend the use of this alternative approach to other materials.

The work presented in this paper was carried out using a cryogenic ICP reactor equipped with in-situ diagnostics. Mass spectrometry measurements enabled to characterize the SF$_6$ physisorption and its surface residence time at different temperatures. Spectroscopic ellipsometry was used to monitor the etching rate and to characterize the sample surface at the nanoscale during the three process steps: SF$_6$ physisorption, pumping and Ar plasma etching. Tests were performed on SiO$_2$, Si$_3$N$_4$ and p-Si coupons glued on SiO$_2$ 6" carrier wafers.

SF$_6$ physisorption experiments will first be presented notably to determine the optimal temperature and purging time for the process. Subsequently, cryo-ALE test results on Si, SiO$_2$ and Si$_3$N$_4$ will be shown. These results will finally be compared to the ones obtained previously using C$_4$F$_8$ physisorption.

This research project is supported by the CERTeM 2020 platform, which provides most of the equipment and funded by the European Union (FEDER fund) as well as the French National Research Agency (ANR PSICRYO fund).

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5:00pm **ALE2-TuA-15 Precision and Repeatability of ALE Process in AlGaN/GaN Layer by in-Situ Etch Depth Monitoring**, ***Sungjin Cho,*** Oxford Instruments Plasma Technology, UK*; M. Loveday,* 1Oxford Instruments Plasma Technology, UK*; A. Newton,* Oxford Instruments Plasma Technology, UK*; D. Cornwell, M. Binetti, T. Zettler,* Laytec AG, Germany

GaN-based hetero structured high-electron-mobility transistors (HEMTs) are key components for the next generation of RF (radio frequency) and high power applications due to their high breakdown field, high-temperature operation, and their strong spontaneous and piezoelectric polarization-induced 2D electron gas (2DEG) of high carrier density and mobility. For safety considerations, normally-off operation HEMTs are vital for power applications. Due to their high gate voltage sweep and low leakage current, gate recessed metal insulator semiconductor (MIS)-HEMTs have been intensively investigated for normally-off operation. But their manufacturing has proven so far too challenging. Among the most significant challenges is sub-nanometer etch monitoring and controlling, to leave a thin (typically under 5 nm) layer of AlGaN, obtaining repeatable device performance.

In this work, we have realized of precision and repeatability of 5nm and 2nm AlGaN left on GaN by in-situ etch depth monitoring. we demonstrate how complementing a relatively slow, low damage atomic layer etch process with monitoring of the remaining AlGaN thickness allows excellent etch depth control of the AlGaN. The AlGaN layer thickness is determined by an AlGaN/GaN-optimized LayTec TRIton^{TM} in-situ UV reflectance metrology tool with ±0.5nm. The accuracy and repeatability of the 2 and 5 nm target depths of AlGaN have been qualified by TEM. All ALE processes were controlled by monitoring the AlGaN depth through the UV reflectance interferometry traces. Furthermore, the UV reflectance results imply that GaN cap and neighbouring AlGaN etch at a varying rate, lower than the reproducible etch rate of bulk AlGaN. The UV reflectance traces clearly resolve the etch steps, which depends on the details of the cyclic ALE process. We have verified the good correlation between AlGaN thicknesses determined by TEM, and in-situ by real-time UV reflectance.

5:15pm **ALE2-TuA-16 Investigation of Self-Limiting Sputtering of Fluorinated Al_2O_3 and HfO_2: Where's the Limit?**, ***Nicholas Chittock****, W. Hoek, S. Balasubramanyam,* Eindhoven University of Technology, The Netherlands*; J. Escandon Lopez, K. Buskes,* ProDrive Technologies, Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, UK*; E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

ALE is becoming increasingly popular due to the high level of etch control and low damage etching it can provide. The use of self-limiting half-cycles for ALE is well-documented, however why and how half-reactions self-limit is less well understood. Such fundamental insight into sputter thresholds and yields is vital information that is missing from the literature for many ALE chemistries. In this work we examine (i) the self-limiting nature of the removal step of anisotropic ALE, (ii) the required energy window and (iii) how the etch rate changes as the material is sputtered.

The sputtering of fluorinated Al_2O_3 and HfO_2 is investigated, where the fluorination is performed by a SF_6 plasma and removal by directional Ar ions. Exploration of surface fluorination goes beyond the widely investigated case of Si ALE by chlorination,[1] providing insight into possible alternative ALE chemistries. To accurately evaluate the minimum energies required for material removal, we utilize tailored waveform (TW) biasing,[2] which allows for improved ion energy control over conventional radio-frequency biasing. The sputter thresholds for Al_2O_3 and HfO_2 were determined to be 59 ± 5 eV and 81 ± 5 eV, respectively. Following modification with an F-based plasma both films were shown to have a decreased sputter threshold, 23 ± 4 eV for Al_2O_3 and 37 ± 4 eV for HfO_2, which opens an ALE window. Additionally, the sputter yield of the modified films is increased as compared to bulk material aiding in removal of the modified layer.

Another important consideration for ALE processing is ensuring that the modified layer can be fully removed. By performing a SF_6 plasma exposure followed by multiple Ar plasma removal steps, we investigated how the layer is removed as a function of Ar plasma exposure time. Initially the etch rate of the modified layer is high, but as the modified layer is removed, the etch rate reduces back to that of bulk material. In our case this suggests the presence of an intermixed AlF_xO_y layer between the surface AlF_3 and bulk Al_2O_3.

Improved understanding of material removal, both in terms of ion energy windows and rate, will facilitate future development of anisotropic ALE processes, and thereby the integration into advanced IC fabrication.

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5:30pm **ALE2-TuA-17 Isotropic Plasma ALE of Al_2O_3 using F-based Plasma and $AlMe_3$: Key Parameters, Upscaling and Applications**, ***Yi Shu,*** Oxford Instruments Plasma Technology, UK*; N. Chittock, E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands*; A. O'Mahony,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands

Isotropic ALE processes are being considered for a range of applications such as controlled thinning of material, smoothing of surfaces, and removal of contaminated or damage surface layers. Although most reported isotropic ALE processes use thermal processes, also plasma-based ones are of recent interest, due to a promise of easier to handle precursors and expanded process parameter space. In our recent work, isotropic plasma ALE of Al_2O_3 was performed using SF_6 plasma and $AlMe_3$, which was demonstrated on a small-scale homebuilt reactor.[1] The $AlMe_3$ dose in the process needs to be sufficient to cause net etching since otherwise AlF_3 deposition is observed.[2] The required $AlMe_3$ dose for net etching will furthermore depend on the degree of fluorination of the various surfaces in the reactor. Therefore, a long and extensive fluorination by the SF_6 plasma could cause challenges in achieving uniform etching with a given $AlMe_3$ dose.

In this contribution we will discuss the transfer of this ALE process to a commercial ALD tool (Oxford Instruments FlexAL) which would also allow process sequences combining ALD and ALE. Depending on the used substrate temperature, plasma dose and precursor dose, either deposition or etching was found to occurred. After obtaining understanding of these parameters, a decent ALE uniformity was achieved (~2% 1-sigma thickness non-uniformity over 150 mm wafer area). Possible applications (e.g., in quantum and power electronics) and parameters to keep in mind for process transfer will be discussed in this contribution.

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