Atomic Layer Etching
Room Plaza Exhibit - Session ALE-SaP

Atomic Layer Etching Poster Session

ALE-SaP-1 Quasi-Atomic Layer Etching of Silicon Nitride with Tunable Directionality and Ultra-high Selectivity, ***Sonam Sherpa***, *A Ranjan,* Tokyo Electron

Self-limiting etch processes have emerged as a viable approach to address the challenges associated with continuous or quasi-continuous plasma processes. To this end, we have previously reported the quasi-atomic layer etching of silicon nitride via sequential exposure to hydrogen and fluorinated plasma[1] . Our work was preceded by Posseme et al. who reported the etching of silicon nitride via exposure to hydrogen plasma followed by dilute hydrofluoric acid (DHF) treatment[2]. Commonality between the two approaches is the increase in reactivity of silicon nitride after the exposure to hydrogen plasma and the underlying assumption was the implantation of hydrogen ions into silicon nitride.

In this talk, we will demonstrate that similar enhancement in reactivity of silicon nitride can also be attained via diffusion of hydrogen atoms into silicon nitride. Comparison of the self-limiting etch via ion-implantation versus diffusion offers new insights into the mechanism for the increase in reactivity of silicon nitride after hydrogen plasma treatment. This process is isotropic and we will demonstrate its feasibility to etch silicon nitride encapsulation layer selective to underlying silicon, silicon oxide, and other materials. These results complement our previous work that reported the anisotropic version of this process[1] and, thus, confirm the realization of self-limiting etch of silicon nitride with tunable directionality and ultra-high selectivity.

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ALE-SaP-2 Atomic Layer Etching with Gas Cluster Ion Beam Irradiation in Reactive Gas Vapor, ***Noriaki Toyoda***, University of Hyogo, Japan; *A Ogawa,* University of Hyogo; *I Yamada,* Univeristy of Hyogo

Atomic layer etchings (ALE) with gas cluster ion beam (GCIB) irradiation in reactive gas vapor were investigated for the first time. Since the kinetic energy of gas cluster ions is shared by thousands of gas atoms or molecules, energy/atoms or energy/molecules can be easily reduced to several eV. As a result, low-damage surface modification is promoted. In additions, since gas cluster ions realize dense energy deposition without severe damage, chemical reaction enhancement at low substrate temperature is expected. By using these characteristics, ALE by GCIB irradiation was studied in this paper. In this study, ALE of Cu films with oxygen GCIB irradiation in acetic acid vapor were investigated. We separated each etching steps as following; (1) adsorption of acetic acid on Cu, (2) evacuation of residual acetic acid vapor, (3) reaction between acetic acid and Cu and subsequent removal of surface Cu layer by oxygen GCIB irradiations. Effects of the following etching parameters on ALE were investigated from real-time Cu thickness on a quartz crystal monitor; acceleration voltage of oxygen GCIB, irradiation time of GCIB, partial pressure of acetic acid, exposure time of acetic acid.

During a one cycle of ALE of Cu with oxygen GCIB in acetic acid vapor, very thin layer of adsorbed acetic acid was formed on Cu surface in the first place. Acetic acid remained on Cu surface after evacuation of residual acetic acid. Subsequently, chemically altered Cu on the surface layer were removed with oxygen GCIB irradiation. In the case of 20 kV oxygen GCIB irradiations, Cu atoms beneath surface layer were also physically sputtered after removal of the chemically modified layer. Consequently, the etching process with 20 kV oxygen GCIB was not self-limiting. It was also observed that there was surface smoothing of Cu by lateral sputtering effects, which arise from physical sputtering of GCIB. On the contrary, surface Cu atoms with adsorbed acetic acid were reactively removed by 5 kV oxygen GCIB as same as the case by 20 kV oxygen GCIB, however, Cu atoms beneath layer were not physically sputtered at 5 kV. Therefore, the etching with 5 kV oxygen GCIB is self-limiting, which is crucial for ALE. Since there are various combination between adsorbed molecules and target materials, it is expected that ALE with GCIB will be applicable for various materials.

ALE-SaP-3 Thermal Atomic Layer Etching of TiO_2 using Sequential Exposures of WF_6 and BCl_3, *P Lemaire,* ***Gregory N. Parsons,*** North Carolina State University

Controlled thin film etching is essential for further development of sub-10 nanometer semiconductor devices. Vapor-phase thermal etching of oxides is appealing for achieving highly conformal etching of high aspect ratio features. We show that tungsten hexafluoride (WF_6) dosing or sequential WF_6 and boron trichloride (BCl_3) exposures can be used for chemical vapor or atomic layer etching (ALE) of oxides. In particular, these processes were observed to selectively etch titania (TiO_2) films versus other oxides including alumina (Al_2O_3) because of different volatility of metal fluorides. The etch process was observed to be temperature dependent, with the etch rate decreasing as the temperature was reduced from 220°C because of reduced volatilization of the metal fluoride and WF_2O_2. XPS shows evidence for a WO_xF_y layer that forms on of the TiO_2 films during the etch process. In addition, the incorporation of BCl_3 enables the volatilization of the WO_xF_y, for controlled etching at lower process temperatures (170°C). Using quartz crystal microbalance (QCM) analysis, we further investigate how the reactant exposure times and process temperature affects the relative etch rate per cycle for the WF_6/BCl_3 process.

ALE-SaP-4 Etch Profile Control of ALD-SiO2 Film Assisted by Alternating ALE Process of Fluorocarbon Deposition and O2 Plasma Etching, ***Masaru Zaitsu,*** ASM, Japan; *T Tsutsumi,* Nagoya University, Japan; *A Kobayashi,* ASM; *H Kondo, M Hori,* Nagoya University, Japan; *T Nozawa, N Kobayashi,* ASM

It is demanded to form not only conformal film by ALD but also any desired shape on patterned structures with the assistance of ALE for advanced devices fabrication. We have recently developed a novel ALE of SiO2 based on alternating process of fluorocarbon deposition and O2 plasma etching, which features saturated etching thickness per cycle for both the fluorocarbon deposition time and O2 plasma etching time. In this time we demonstrate the profile control of ALD SiO2 film by controlling etch conformality of this ALE process.

Conformal SiO2 film is deposited on a Si trench by plasma-enhanced ALD and then followed by the ALE with 60 MHz CCP type etching chamber. We investigate the etch conformality (EC) which is defined as the ratio of the etched thickness of sidewall film and that of top film with varying the ALE process parameters. A standard condition results EC of 33% as shown in Figure 1, which shows relatively anisotropic etching. On the other hand, a different condition using Ar/O2 as the etching plasma gas instead of O2 plasma shows EC of >100%, where sidewall film is etched while almost no etching on top film. This is because more carbon polymer is formed only on top due to anisotropic ion bombardment and it prevents etching top SiO2 film. EC can be controlled depending on plasma gas and further tuned by varying process parameters such as pressure, RF power, and substrate bias.

ALE-SaP-5 *In Situ* Mass Spectrometer Studies of Volatile Etch Products During Thermal Al_2O_3 Atomic Layer Etching Using HF and Trimethylaluminum, ***Joel Clancey***, *S George,* University of Colorado - Boulder

The technique for removing atomic layers using sequential, self-limiting reactions known as atomic layer etching (ALE) offers a new level of etching precision. This atomic precision is needed by the semiconductor industry as advanced devices continue to scale to the 10 nm technology node and beyond. Thermal ALE using sequential, self-limiting reactions is emerging as a new technique capable of isotropically etching challenging 3D and high aspect ratio device architectures.

Thermal ALE has been developed for Al_2O_3, HfO_2, ZrO_2, ZnO and AlN based on sequential fluorination and ligand-exchange reactions. For many of these ALE systems, the surface reactions during thermal ALE have been characterized by *in situ* quartz crystal microbalance (QCM) and FTIR spectroscopic measurements [1, 2]. These studies have identified the mass changes and surface species during thermal ALE. The volatile etch products have also been inferred based on the mass changes and surface species. However, these volatile etch products have not been directly confirmed using mass spectrometry.

In this presentation, we describe a new ALE reactor with an *in situ* quadrupole mass spectrometer (QMS) with high resolution and mass range. A schematic of this new ALE reactor is given in the supplemental figure. This new apparatus is then used to investigate the thermal ALE of Al_2O_3 using HF and trimethylaluminum (TMA) as the reactants [1]. We can identify the volatile etch products during each HF and TMA reaction. The volatile etch products for the fluorination and ligand-exchange reactions evolve during the reactant exposures and present some surprises.

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ALE-SaP-6 Cyclic Plasma Cleaning Process of SiO_2 Layers using Surface Fluorination*, **Kyongbeom Koh**, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Controlling impurities and particles is an important factor in determining the performance and yield of semiconductor devices. However, it becomes more challenging as the critical dimension shrinks. Many contaminants such as organic materials, inorganic materials and native oxide are generated in etching process. Among them, especially, native oxide can have an adverse effect on electronic devices. It can create higher contact resistance, which makes the IC inoperable. Other disadvantages of native oxide involve leakage current on gate oxide and inadequate formation of silicide in devices.[1] Various wet cleaning processes are mainly applied to remove the native oxide.[2-3] However, the conventional wet cleaning processes start show limitations in some applications. Therefore, various dry cleaning processes are actively being investigated in order to overcome the limitations of the wet cleaning processes in nanoscale patterns.[4]

In this work, cyclic plasma process was studied for SiO_2 (native oxide) removal with surface fluorination in an inductively coupled plasma (ICP) reactor with CHF_3, CF_4, Ar, O_2 chemistries. The cleaning rate of cyclic process was found to be lower than that of direct process, so we studied cyclic process for SiO_2 cleaning than direct process. The cyclic plasma cleaning process is composed of two steps. The first one is fluorination of SiO_2 surface by fluorocarbon radicals which are generated from CHF_3 or CF_4 plasmas. The other step is removal of fluorinated SiO_2 layers by ions and radicals which are generated from O_2 or Ar plasmas. Formation of fluorocarbon layer on SiO_2 surface was confirmed by SEM and XPS analysis. Cleaning rate was investigated by varying bias voltage and ion density by monitoring processes with a VI probe and an ion monitor. It is also confirmed that the cleaning rate becomes self-limited as the fluorination and cleaning time increase. Cleaning rates were compared at various process conditions and the cleaning rate could be controlled under 10 Å/cycle.

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Keywords: Cyclic plasma cleaning, native oxide, surface fluorination

ALE-SaP-7 Low Damage Cyclical Etching of GaN and AlGaN*, A Goodyear,* Oxford Instruments Plasma Technology, UK*; P Abrami,* University of Bristol, UK*; **Mike Cooke**,* Oxford Instruments Plasma Technology, UK*; M Loveday,* Oxford Instruments Plasma Technology

The AlGaN gate recess etch requires the removal of a controlled amount of material, up to 30nm thick, with minimal disruption to the few nanometres remaining in the layer. Other device structures call for etching GaN, without disrupting underlying AlGaN. We have studied the use of cyclical ALE-style etch processes for these materials.

We find that both materials etch at around 1.5-4 Å /cycle in a Cl_2/Ar cycle, similar to that used for ALE of silicon^1, in an Oxford Instruments PlasmaPro100 Cobra^{300} ICP etch tool modified for ALE^2. The baseline of the cycle, using a continuous ICP plasma is:

10 – 100 msec chlorine dose; the dose can also be varied by changing the flow

2 – 20 seconds of purge

3 – 30 seconds of 13.56MHz RF bias at 0 – 50 Vdc self bias

We present graphs showing a synergistic effect of gas dose and ion bombardment, and a distinct plateau in etch per cycle v chlorine dose for both GaN and AlGaN. The synergy is seen by comparing the etch per cycle with and without a chlorine dose. Zero etching is observed if only the dose step is applied. Only a slight saturation behaviour in etch per cycle v etch step intensity (bias voltage or time) was observed, due to a low selectivity of etch rate under argon ion bombardment, between chlorinated and non-chlorinated surfaces. The etch step bias required to consume all the adsorbed reactant is very close to the onset of physical sputtering of the base material, so that no plateau is seen. The cyclical etch strategy provides a repeatable low etch rate using minimal ion energies, although it does not give a significant selectivity between GaN and AlGaN, using this chemistry.

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ALE-SaP-8 Thermal Atomic Layer Etching of ZnO by "Conversion-Etch" Using Hydrogen Fluoride and Trimethylaluminum*, **David Zywotko**, S George,* University of Colorado - Boulder

ZnO atomic layer etching (ALE) was demonstrated using hydrogen fluoride (HF) and trimethylaluminum (TMA) as the reactants [1]. ZnO thin films were grown by ZnO atomic layer deposition (ALD) at 150°C using diethylzinc (DEZ) and H_2O. The ZnO films were then etched using sequential exposures of HF and TMA. *In situ* quartz crystal microbalance (QCM) monitored the linear mass loss during etching at 265°C. The QCM also allowed for analysis of individual mass gains and losses during reactant exposures. In addition, ZnO ALD films were grown on Si(100) wafers for *ex situ* analysis. The ZnO ALE was measured between 205°C and 295°C using spectroscopic ellipsometry and x-ray reflectivity analysis . The etch rate was temperature dependent and varied from 0.01 Å/cycle at 205°C to 2.19 Å/cycle at 295°C.

The QCM measurements at 265°C showed that the sequential HF and TMA thermal reactions were self-limiting. In addition, the large mass loss during the TMA exposures could not be explained by simple ligand-exchange reactions that remove the AlF_3 fluoride layer following fluorination by the HF exposure. Instead, the large mass loss suggested that TMA was converting the ZnO surface to an Al_2O_3 layer. The HF then is believed to fluorinate the Al_2O_3 surface to an AlF_3 layer. Subsequently, the TMA exposure removes the AlF_3 layer by ligand-exchange reactions before continuing to convert more ZnO to Al_2O_3. This new strategy for thermal ALE can be called a "conversion-etch" mechanism.

The conversion of ZnO to Al_2O_3 during ZnO ALE may be one example of a fairly general phenomena. Conversion reactions may occur when the metal precursor used for ligand-exchange can form a metal oxide that is more stable than the initial metal oxide. These conversion reactions may be very useful in thermal ALE. For example, the conversion reaction could convert a metal oxide that has a volatile fluoride and would not display self-limiting fluorination to another metal oxide that may have a stable fluoride. The conversion reaction could also convert a metal oxide that may not have a volatile reaction product after ligand-exchange to another metal oxide that may have a volatile reaction product.

[1] David R. Zywotko and Steven M. George, "Thermal Atomic Layer Etching of ZnO by a "Conversion-Etch" Mechanism Using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum", *Chem. Mater.* **2017**- DOI: 10.1021/acs.chemmater.6b04529.

ALE-SaP-9 Cryogenic Atomic Layer Etching of SiO_2*, N Holtzer, **Thomas Tillocher**, P Lefaucheux, R Dussart,* GREMI Université d'Orléans/CNRS, France

Atomic Layer Etching (ALE), that has been developed in the 90s, addresses new challenges in micro and nanoelectronics where high precision processes are required. This is typically a sequential process relying on a self-limited reaction of radicals created in the plasma phase and adsorbed on the material to be etched. Precursor radicals adsorb ideally on the first monolayer. Then, under a low energy ion bombardment, the etch products form and desorb until the adsorbed layer is depleted (self-limited reaction). This removes a few monolayers. By repeating the cycle, the material is etched monolayers by monolayers.

ALE of SiO_2 has already been demonstrated with a 3-step process. The first step is an Ar/C_4F_8 plasma with no RF self-bias voltage applied to the substrate holder. The oxide surface is then coated with a very thin fluorocarbon (FC) layer. The second step is a pure Ar plasma still with no RF self-bias voltage used to pump C_4F_8 out of the chamber. The third and final step is an Ar plasma with about 10V RF self-bias voltage. The ion energy must be kept below the sputtering threshold. If the thickness of the FC layer is accurately controlled, the process can be self-limited.

Such a process has been implemented and investigated on our ICP etching tool. It is observed that it is not reproducible since, depending on chamber wall conditions, it can switch from an etching regime to an unwanted deposition regime. A sequential 4-step process is proposed instead: after the etching step (step 3), an O_2-based cleaning plasma step is added and improves overall process reproducibility. The chamber itself, whereas it provides gas pulsing capability for alternated processes, requires very accurate control of gas flows to reach self-limiting etching and hence low thickness etched per cycle. Ultimately, an etch rate of 0.3 A/cycle has been obtained in our experimental conditions.

However, fluorocarbon contamination of chamber walls is an issue. We propose to run ALE at cryogenic temperature of the substrate as a potential solution. Different precursor chemistries are investigated (fluorine-based, fluorocarbon-based) for top layer adsorption. At such a low temperature, species are adsorbed only at cooled surface and hence wall pollution is mainly suppressed. In addition, the substrate temperature is expected to be an additional process knob that enables the adjustment of the adsorbed precursor layer thickness and hence the reduction of the etched thickness per cycle. Finally, since radical diffusion in the bulk material is reduced at cryogenic temperature, low structural damage is expected as well.

ALE-SaP-10 SF_4 as a New Fluorine Reagent for Thermal ALE: Application to Al_2O_3 and VO_2 ALE*, **Jonas Gertsch**, N Johnson, V Bright, S George,* University of Colorado - Boulder

Thermal ALE has been demonstrated recently for many materials including Al_2O_3, HfO_2, ZrO_2, ZnO, and AlN using fluorination and ligand-exchange reactions [1]. The fluorine reagent for the fluorination reactions has been HF from an HF-pyridine solution. HF-pyridine is a safer HF source than anhydrous HF. However, safety concerns, as well as the need for a stronger fluorination source, have motivated an exploration of SF_4 as the fluorine reagent.

This study examined Al_2O_3 and VO_2 ALE using SF_4 for fluorination together with $Sn(acac)_2$ (tin(II) acetylacetonate) as the metal precursor for ligand-exchange. Al_2O_3 and VO_2 ALD films were grown at 150 °C using trimethylaluminum and H_2O for Al_2O_3 ALD and tetrakis(ethylmethylamido) vanadium(IV) and H_2O for VO_2 ALD. These films were then etched using sequential SF_4 and $Sn(acac)_2$ exposures. An *in situ* quartz crystal microbalance was employed to monitor film growth and etching during the ALD and ALE reactions. *Ex situ* X-ray reflectivity (XRR) and spectroscopic ellipsometry (SE) were used to characterize film thicknesses on silicon substrates before and after etching.

The Al_2O_3 and VO_2 ALD films were removed with a linear etch rate of ~0.2 Å/cycle and ~0.3 Å/cycle, respectively, at 200°C. Both SF_4 and $Sn(acac)_2$ exhibited self-limiting reactions on Al_2O_3 and VO_2. The temperature dependence was also explored for Al_2O_3 ALE using SF_4 and $Sn(acac)_2$. The etch rates varied from 0.03 Å/cycle at 150 °C to 0.3 Å/cycle near 250 °C. To replace $Sn(acac)_2$, BCl_3 (boron trichloride) has also been explored as an alternative for VO_2 etching together with SF_4. Initial results have shown that BCl_3 and SF_4 can etch VO_2 by a "conversion-etch" mechanism [2]. BCl_3 is thought to convert the VO_2 surface to a B_2O_3 layer. SF_4 can then spontaneously etch the B_2O_3 surface layer.

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ALE-SaP-11 Demonstrating Manufacturability of Atomic Level Etch (ALE) through Accelerated Neutral Atom Beam (ANAB) Processing*, **Daniel Steinke**, B Sapp, S PapaRao,* SUNY Polytechnic Institute*; E Barth,* SEMATECH*; V Kaushik, M Rodgers, C Hobbs,* SUNY Polytechnic Institute*; M Walsh, S Kirkpatrick, R Svrluga,* Neutral Physics Corporation

Accelerated Neutral Atom Beam (ANAB) processing has been shown to be an effective method to achieve ALE in a cyclic process when combined with a selective removal step to form a SiN spacer [Barth *et al*, ALE Workshop 2016]. In this paper, we present the progress towards demonstrating manufacturability of the ANAB-enabled ALE process – in terms of factors such as process speed, control and stability, and ease of integration into a standard 300mm fabrication facility. In this work we will show several-fold improvement of wafer throughput by reduction of ANAB process times while still accomplishing the necessary surface modification by ANAB exposure. A detailed investigation of the applicability of various processes for the selective removal portion of the ALE cycle has shown that ANAB effectively reduces the surface roughness that is introduced by the selective removal process step. We also demonstrate the ability to affect the sidewall profile of the spacer etch by adjusting the ANAB process parameters throughout the cycled process, such as average neutral atom energy, the incorporation of chemically active species into the ANAB beam, etc. These improvements, combined with the installation of the first ANAB tool in the state of the art 300mm process line at the College of Nanoscale Science and Engineering (CNSE), are aiding wider implementation of ANAB-based ALE in semiconductor manufacturing lines.

ALE-SaP-12 Etching with Low Te Plasmas*, **Scott Walton**, D Boris,* U.S. Naval Research Laboratory*; S Hernández,* U.S.Naval Research Laboratory*; H Miyazoe, A Jagtiani, S Engelmann, E Joseph,* IBM TJ Watson Research Center

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. The appropriate threshold and process windows are certainly material specific but it is reasonable to assume many applications require low energy ions. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{11} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical concentration compared to discharges. As such, these sources are well-suited to explore processing space not commonly found in industrial tools. In this work, we discuss SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds. We pay particular attention to the etch rates, selectivity (vs. carbon films, Si and SiO_2), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. These results are compared with plasma diagnostics to gain a better understanding of the process requirements and windows for threshold etching of SiN. This work is partially supported by the Naval Research Laboratory base program.

ALE-SaP-13 Surface Cleaning of Gallium Antimonide Oxides: The Role of Hydrogen Atoms, Argon Ions, and Temperature*, **Thomas Larrabee**, S Prokes,* Naval Research Laboratory

Complete removal of surface oxides from GaSb and other III-V semiconductors may be accomplished by a variety of means, including thermal oxide desorption at high temperature, chemical reaction with atomic or molecular hydrogen, and physical sputtering by noble gas ion bombardment. It is often difficult to remove the oxide while preserving a low-defect surface, which is typically critical to limit Fermi-level pinning that degrades device performance, because one species desorbs faster than another or because the temperatures or ion energies involved cause physical surface defects. Plasmas, however, particularly mixtures of argon and hydrogen, have been shown to work well in surface preparation of GaSb interfaces at very low temperature.(1) What is not known clearly is which species of the plasma is the most critical, how low the temperature can be to effectively remove oxide, or whether there is a *synergistic* effect to multiple species in atomic layer surface cleaning at low temperature. To investigate this phenomenon, GaSb (001) surfaces have been prepared in an UHV chamber with in-situ photoelectron spectroscopies and low-energy electron diffraction (LEED).(2) The effects of atomic hydrogen exposure alone, low- and moderate-energy Ar+ ions alone, and *simultaneous* atomic hydrogen and low-energy Ar+ ions (like would be encountered in many plasma systems) on oxidized GaSb will be presented. The effectiveness of oxide stripping and re-oxidation has been evaluated with surface-sensitive electron-stimulated Auger spectroscopy and XPS, and has been studied as a function of temperature. LEED patterns confirm the ordering and crystallinity that may still be achieved, even after multiple oxidations and oxide removals. Controlled oxidation and selective, damage-free oxide stripping will also be explored as a route to a pseudo atomic layer etch process for GaSb. Such a process could be sped up considerably in plasma-based reactor at higher pressures, when the requirements on the plasma, such as ion energy and flux, hydrogen atom flux, and surface temperature are understood.

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ALE-SaP-14 Aluminum Native Oxide Surface Cleaning and Passivation in an Atmospheric Plasma System*, **John Mudrick**, M Pohl, K Knisely,* Sandia National Laboratories

Plasma cleaning is an integral part of electronics processing used for surface decontamination, wire bonding, wafer-to-wafer interconnect formation, preparation for film growth, and many other process steps. Plasma cleaning and passivation of aluminum is of particular importance because any degree of ambient exposure results in a rapidly-forming native oxide several nanometers in thickness, potentially deteriorating the electrical and morphological properties of the Aluminum surface. Careful control of this oxidized surface at the atomic scale is of paramount importance for many steps. In this work we use a flexible, low-damage dielectric barrier discharge atmospheric plasma treatment system to fully reduce oxidized aluminum surfaces and passivate against future re-oxidation. Wire bond pull tests and water contact angle (WCA) measurements were used to initially characterize the aluminum cleaning process. Aluminum wire bonds made to an untreated aluminum surface failed under a force of (10.1 ± 1.8) grams. Exposing the aluminum surface to a hydrogen-based plasma prior to wire bonding resulted in an increased bond strength, requiring a force of (13.2 ± 0.9) grams for failure. WCA measurements correlate this enhancement with native oxide removal: untreated aluminum samples show a weakly hydrophilic surface with a contact angle of (57 ± 2) degrees. Exposing the samples to the same hydrogen-based plasma reduces the WCA to (28 ± 5) degrees, suggesting the degree of oxidation is reduced. Further increasing the plasma exposure time results in a steady decrease in WCA until the native oxide is completely removed, Fig. (a) and (b). However, the WCA increases rapidly under ambient exposure. To combat this re-oxidation, nitrogen gas is added to the plasma in order to passivate broken Al-O bonds and improve process flexibility. Both mixed mode – hydrogen and nitrogen mixed gas flow - and sequential – separate hydrogen and nitrogen steps – passivation schemes are investigated in order to maximize the time with minimal WCA. Both schemes show improved resistance to aluminum re-oxidation. To date, best passivation is achieved in continuous mode: a modest WCA increase from 2 to 5 degrees is observed after 180 minutes of re-oxidation in cleanroom ambient conditions, Fig. (c). Cleaning and passivation mechanisms will be further characterized with x-ray photoelectron spectroscopy measurements. Extensions to aluminum nitride film growth on plasma-cleaned and passivated aluminum substrates are also underway.

ALE-SaP-15 Atomic Layer Etching in Reactive Ion Etching System for Nanoscale Pattern Transfer*, S Khan,* ***Dmitry Suyatin****, M Graczyk, A Kvennefors,* Lund University, Sweden*; E Kauppinen,* Aalto University, Finland*; M Huffman, I Maximov,* Lund University, Sweden*; J Sundqvist,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

Today the characteristic size of advanced electronic components is already below 20 nm, which corresponds to less than 40 silicon atoms. Atomic Layer Etching (ALE) provides atomic precision material removal and is inherently a damage-free etch process. This makes ALE to be very important for fabrication of leading edge electronic components [1-3].

Here we present our study of ALE process in Plasmalab-100 etch system from Oxford Instruments for nanoscale pattern transfer. The ALE process for Si was based on surface activation with Cl_2 gas and removal of the activated layer in Ar plasma [4]. Nanoscale patterns with different geometries and feature sizes, see Figure 1, were fabricated with electron beam lithography in HSQ (hydrogen silsesquioxane) resist. Inspection of the nanoscale patterns after ALE allowed us to study different effects and limitations of the ALE process, for example loading, trenching and sidewall tapering.

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ALE-SaP-16 Selective Fluorocarbon-based Atomic Layer Etching in a Conventional Parallel-Plate, Capacitively Coupled Plasma*,* ***Stefano Dallorto****,* Ilmenau University of Technology*; A Goodyear, M Cooke,* Oxford Instruments Plasma Technology, UK*; S Dhuey, A Schwartzberg, S Sassolini,* Lawrence Berkeley National Laboratory*; C Ward,* Oxford Instruments*; D Olynick,* Lawrence Berkeley National Laboratory*; I Rangelow,* Ilmenau University of Technology*; S Cabrini,* Lawrence Berkeley National Laboratory

We study a Fluorocarbon(FC)-based ALE process for controlling the etching of several substrates at the atomic level in a conventional parallel-plate, capacitively coupled plasma tool. In a steady state Ar plasma, a periodic fluorocarbon gas injection enables control of the deposited FC layer thickness in the one to several Angstrom range and chemical modification of the surface. For low energy Ar^+ ion bombardment conditions, the physical sputter rate of the substrate vanishes, whereas the modified surface can be etched when FC reactants are present at the surface.

With the goal of achieving high selectivity FC-based ALE, we study the etching of different materials under different FC chemistry. Etching rate per cycle is first investigated using spectroscopy ellipsometer on unpatterned surfaces. Using CHF_3-based ALE for SiO_2 etching, the etching rate is 8.5Å/cycle. SiO_2 features with different critical dimensions has been etched under different conditions. The SiO_2 features etched using an ALE process (Row 1) are aspect-ratio independent compared to the features obtained with a continuous RIE process (Row 2). It is worth noticing how the results change when higher DC bias is used in the etch step of the ALE process (Row 3). This case is dominated by sputter etching with results in a high degree of physical/ionic etching.

A successful application of the cyclic ALE approach has been demonstrated. Overall, the cyclic FC/Ar etch has proven to pattern features well (Row 1), with great potential for significant improvement in overall etch performance.

ALE-SaP-17 RF Plasma Electrostatics: The Influence on Film Morphology and Carbon Incorporation*,* ***K. Scott Butcher****,* Meaglow Ltd, Canada*; P Terziyska,* Institute of Solid State Physics, Bulgarian Academy of Sciences, Bulgaria*; V Georgiev,* Meaglow Ltd, Canada*; D Georgieva,* Semiconductor Research Lab, Lakehead University, Canada*; R Gergova,* Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, Bulgaria*; P Binsted, S Skergetc,* Semiconductor Research Lab, Lakehead University, Canada

RF plasmas have a DC component that can affect the migration of species deposited during film deposition. Electrostatic interactions between the positive charge presented by RF plasmas and the negative charge of deposited layers can have a strong influence on film morphology. We have characterised some of these interactions and published some results that may be of interest [Butcher et al. J. Appl. Phys. **121** (2017) 013301].

Electrostatic field interactions can also play a strong role in reducing carbon contamination, we provide an example of GaN where carbon contamination using a nitrogen plasma is reduced below detection limits using controlled electrostatic interactions.

ALE-SaP-18 Atomic Layer Etching of Amorphous Silicon with Selectivity Towards MoS_2*,* ***Markus Heyne****,* KU Leuven, Belgium*; A Goodyear,* Oxford Instruments Plasma Technology, UK*; J de Marneffe,* IMEC, Belgium*; M Cooke,* Oxford Instruments Plasma Technology, UK*; I Radu,* IMEC, Belgium*; E Neyts,* University of Antwerp, Belgium*; S De Gendt,* KU Leuven, Belgium

Transition-metal dichalcogenides and their heterostructures enable promising architectures for novel device concepts. Nowadays, prototype structures are fabricated by manual stacking of exfoliated nanosheets or transferred CVD layers. This transfer approach has the advantage of reducing processing steps being detrimental to the sensitive 2D materials. However, it cannot be automated and it is not compatible with the geometrical scaling required for advanced CMOS applications. The exploration of selective patterning and selective growth is therefore essential to build heterostructures with defined geometries and electrical contacts to the individual nanosheets.

This paper describes the first critical step to fabricate a WS_2/MoS_2 heterostructure by selective conversion of sacrificial Si [1]. Large-area MoS_2 as the bottom MX_2 layer is deposited by sulfidation [2,3] and pre-patterned by optical lithography and conventional etch. Amorphous Silicon (aSi) is deposited on top of the MoS_2 and optical lithography is performed defining the top layer of the heterostack, which is converted to WS_2 [1]. The key part of the device prototyping is the selective etch of aSi without damage to the underlying MoS_2. To this end, we investigated an atomic layer etching (ALE) process based on Cl_2 plasma chemistry in an Oxford Instruments PlasmaPro 100 ICP reactor equipped with an ALE kit. The process was composed of alternating cycles of a Cl_2 pulse followed by low-bias Ar activation in a continuous ICP mode. The controllable silicon etch rate of the ALE process was 0.6 nm per cycle. The process stopped on the MoS_2 without degradation of its structure, enabling very high overetch. The exposed MoS_2 quality was characterized by Rutherford backscatter spectrometry, Raman spectroscopy, and X-ray photoelectron spectroscopy. No damage to the MoS_2 was detected. Finally, the developed aSi ALE with selectivity to MoS_2 was applied to samples with lithography patterns to demonstrate the applicability for pattern transfer. The presented work also covers the challenges of applying ALE to 2D materials, and focuses on the detrimental influence from adsorbed water on the carrier wafer and chamber walls, and the protecting effect of the heterostack's top layer during the plasma ignition. The established procedure opens a path to study the plasma-surface interaction on MX_2 materials without damaging the top molecular MoS_2 layer.

[1] M. Heyne et. al, Nanotechnology **28**, 04LT01 (2017)

[2] M. Heyne et. al, J. Mater. Chem. C **4**, 1295 (2016)

[3] D. Chiappe et al., Advanced Materials Interfaces **3(4)**, 1500635 (2016)

ALE-SaP-19 Simulation of New Material-Systems for Directional Atomic Layer Etching*, **Ivan Berry**, K Kanarik, T Lill, V Vahedi, R Gottscho,* Lam Research Corp.

Atomic layer etching (ALE) has recently been introduced into manufacturing of 10 nm logic devices. ALE is an etching technology that deploys separated and self-limited steps. In directional ALE, at least one of the two steps has to be directional, i.e., has to transfer momentum to the surface and/or be sensitive to line of sight. Ion bombardment is most commonly used to realize directional ALE. ALE exhibits the same ion-neutral synergy as RIE but the removal amount is not flux dependent due to the separation of the neutral (chemical) and ion fluxes /1,2/. Flux independence gives ALE its most important property: inherent uniformity across all length scales – across wafer, loading, ARDE and surface smoothness. As compared to conventional plasma etching, the separate steps in ALE also offers a simplified system in which to study the basic etching mechanisms. For example, recently, the process window of ALE was shown to be predictable based on the energy barriers relevant to the substrate-reactant combination, such as the surface binding energies of the chemically modified and bulk material /3/. The separate and independent steps make it particularly suitable to modelling efforts. Here we present the latest results in feature scale modelling of new material systems amenable to the ALE approach.

[1] H.F. Winters, J.W. Coburn, E. Kay, J. Appl. Phys. 48, 4973 (1977)

[2] K.J. Kanarik et al., J. Vac. Sci. Technol. A 33(2) (2015)

[3] K.J. Kanarik et al., J. Vac. Sci. Technol. Submitted Dec 2016

Sunday Afternoon, July 16, 2017

Atomic Layer Etching
Room Plaza D - Session ALE-SuA

Atomic Layer Etching Session I (1:30-3:30 pm) and II (4:00-5:30 pm)

Moderators: Geun Young Yeom, Sungkyunkwan University, Korea, Satyarth Suri, Intel Corporation, Ankur Agarwal, KLA-Tencor

1:30pm **ALE-SuA-1 Atomic Layer Processes to Enable the Atomic Scale Era**, ***Robert Clark***, *K Tapily, J Smith, N Mohanty, S Kal, D Newman, S Consiglio, D O'Meara, K Maekawa, A Mosden, A deVilliers, P Biolsi, T Hurd, C Wajda, G Leusink,* TEL Technology Center, America, LLC **INVITED**

As Figure 1 below demonstrates, the implementation of FinFETs at the 22nm node introduced a new minimum patterned feature size, fin half pitch, into CMOS high volume manufacturing. In addition, the 22nm node marked the initial use of self-aligned multiple patterning for CMOS features, which was required in order to pattern features below the limit of resolution of 193nm immersion (193i) lithography. At the 14nm node Intel's patterned fin feature size fell below 100 atoms in width, marking the beginning of what can be termed the atomic scale era in CMOS manufacturing.[1] Continued scaling is expected to drive all of the critical feature sizes below 100 atoms wide in the near future for CMOS and memory devices as well. Considering features in terms of atoms illuminates a fundamental roadblock to continuing linear scaling: atoms do not scale.

Depositing and etching films used to manufacture atomic scale devices requires atomic level control. Atomic layer deposition and etch (ALD and ALE), including quasi-ALD and quasi-ALE, processes are therefore finding increasingly more use within semiconductor manufacturing. Patterning and aligning features below the lithographic limit requires clever process designs and the inherent control, conformality, and uniformity afforded by ALD and ALE. Likewise, depositing and etching functional films which are in many cases an order of magnitude thinner than the smallest feature sizes can only be controlled using ALD and ALE. Highly selective ALD and ALE processes including area and material selective processes, as well as anisotropic depositions and etches are sought to reduce the reliance and overburden needed for chemical mechanical planarization (CMP) in order to realize bottom up alignment. In this talk we will describe the challenges driving ALD and ALE into manufacturing and provide examples of how we are meeting those challenges with processes that will enable scaling to the 3nm node and beyond.

Figure 1. Historical and Projected Atomic Feature Sizes (half pitch/0.235 nm/Si atom) in CMOS High Volume Manufacturing. Projected feature sizes are based on Intel historical trend

S. Natarajan *et al*, IEDM Tech Dig., pp. 71-73, 2014.

2:00pm **ALE-SuA-3 Thermal Atomic Layer Etching of SiO_2 by a "Conversion-Etch" Mechanism**, *J DuMont, A Marquardt, A Cano,* ***Steven M. George,*** University of Colorado

SiO_2 is an important semiconductor material and SiO_2 etching is needed in many steps during semiconductor manufacturing. SiO_2 atomic layer etching (ALE) has been demonstrated earlier using periodic exposures of C_4F_8 plasma synchronized with Ar^+ ion bombardment [1]. In this work, we report a thermal process for SiO_2 ALE based on sequential exposures of trimethylaluminum (TMA) and hydrogen fluoride (HF) at 300°C. The etching mechanism involves the conversion of SiO_2 to Al_2O_3/aluminosilicate by TMA and the subsequent etching by sequential fluorination and ligand-exchange reactions [2].

Ex situ x-ray reflectivity measurements revealed that the etch rate was dependent on reactant pressure. SiO_2 etch rates of 0.027, 0.15, 0.20, and 0.31 Å/cycle at 300°C were observed at reactant pressures of 0.1, 0.5, 1.0 and 4.0 Torr, respectively. *Ex situ* spectroscopic ellipsometry measurements agreed with these etch rates versus reactant pressure. *In situ* Fourier transform infrared (FTIR) spectroscopy investigations also observed SiO_2 etching that was dependent on reactant pressure. The FTIR studies showed that the TMA and HF reactions displayed self-limiting behavior. In addition, the FTIR spectra revealed that an Al_2O_3/aluminosilicate intermediate was present after the TMA exposures.

The Al_2O_3/aluminosilicate intermediate is consistent with a "conversion-etch" mechanism where SiO_2 is converted by TMA to Al_2O_3, aluminosilicates and reduced silicon species. *Ex situ* x-ray photoelectron spectroscopy (XPS) studies confirmed the reduction of silicon species after TMA exposures. Following the conversion reaction, HF can fluorinate the Al_2O_3 and aluminosilicates to species such as AlF_3 and SiO_xF_y. Subsequently, TMA can remove the AlF_3 and SiO_xF_y species by ligand-exchange reactions and then convert additional SiO_2 to Al_2O_3. Other conversion reactions may be helpful to transform various materials that cannot be directly etched to different materials that can be etched using thermal ALE.

[1] D. Metzler, R.L. Bruce, S. Englemann, E.A. Joseph and G.S. Oehrlein, "Fluorocarbon Assisted Atomic Layer Etching of SiO_2 Using Cyclic Ar/C_4F_8 Plasma", *J. Vac. Sci. Technol. A* **32**, 020603 (2014).

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

2:15pm **ALE-SuA-4 The Challenges and Opportunities in Plasma Etching of Functionally Enhanced Complex Material Systems**, ***Jane Chang,*** UCLA **INVITED**

The introduction of new and functionally improved materials into silicon based integrated circuits is a major driver to enable the continued down-scaling of circuit density and performance enhancement in analog, logic, and memory devices. The top-down plasma enhanced reactive ion etching has enabled the advances in integrated circuits over the past five decades; however, as more etch-resistive materials are being introduced into these devices with more complex structures and smaller features, atomic level control and precision is needed in selective removal of these materials. These challenges point to the growing needs of identifying and developing viable etch chemicals and processes that are more effective in patterning complex materials and material systems such as multiferroics, magnetic materials and phase change materials.

In this talk, a generalized approach based on combined thermodynamic assessment and kinetic validation is presented to identify and validate the efficacy of various plasma chemsitries. Specifically, potential reactions between the dominant vapor phase/condensed species at the surface are considered at various temperatures and reactant partial pressures. The volatility of etch product was determined to aid the selection of viable etch chemistry leading to improved etch rate of reactive ion etching process. Based on the thermodynamic screening, viable chemistries are tested experimentally to corroborate the theoretical prediction. Some of the above mentioned material systems such as magnetic materials used in non-volatile memory devices are used as examples to demonstrate the broad applicability of this approach.

2:45pm **ALE-SuA-6 A Novel Process for Atomic Layer Etching of ZnO using Acetylacetone and Remote O_2 Plasma**, ***Alfredo Mameli,*** *M Verheijen, A Mackus, W Kessels, F Roozeboom,* Eindhoven University of Technology, Netherlands

Along with the drive for anisotropic processes of Atomic Layer Etching (ALE) there is interest in isotropic counterparts.[1] Therefore, in this work, we demonstrate a novel plasma-assisted ALE process for ZnO which is driven by radicals and therefore anticipated to be isotropic. The process consists of alternating doses of acetylacetone (Hacac) and O_2 plasma, interleaved by Ar purges steps. It is expected that Hacac forms volatile complexes by metal oxide surface chelation (e.g. $Zn(acac)_2$), whereas the O_2 plasma is used as a cleaning step to remove unreactive precursor fragments and to reset the surface for the next etching cycle[2]. This hypothesis is supported by a synergy test of the ALE process, which proved that only the alternated doses of Hacac and O_2 plasma led to etching, whereas neither Hacac, nor O_2 plasma alone resulted in ZnO etching.

The ZnO layer thickness measured by *in-situ* and *ex-situ* ellipsometry was found to decrease linearly with the number of cycles with an etch per cycle (EPC) of ~0.08 nm/cycle. This was corroborated by *ex-situ* FTIR and X-ray diffraction measurements. The ALE process was tested over a range of temperatures between 150 and 300°C. X-ray photoelectron spectroscopy demonstrates that the ZnO stoichiometry is preserved throughout the etching process, without any contamination of the film. The same ALE process was also used for etching other metal oxides such as CuO_x, Al_2O_3 and In_2O_3 yielding EPC values in a range between 0.01 and 0.08 nm/cycle. Furthermore, we demonstrate that this ALE process is selective over SiO_2. This was demonstrated by locally depositing SiO_2 on top of the ZnO to serve as a hard mask for the etching. The selectivity stems from the fact that Hacac does not chemisorb on SiO_2 as demonstrated by independent wet chemistry experiments and FTIR measurements conducted on the ZnO and SiO_2 powders. Finally, we will discuss the influence of the starting material properties, as preliminary investigations indicated that the crystallinity of the material to be etched can affect the EPC.

We believe that this novel plasma assisted-ALE process can be extended to other materials. This chemistry does not involve halogens or halides, which minimizes potential contamination issues. It is important to realize that this ALE chemistry gives selectivity for a different set of materials as compared to halide-based isotropic ALE processes, and therefore represents a valuable addition to the ALE toolbox.

[1]Zywotko, D. R. *et al.*, Chem. Mater. **29**, 1183 (2017)

[2]George, M. A.,*J. Electrochem. Soc.,***143**, 3257 (1996)

3:00pm **ALE-SuA-7 Determining the Benefits and Limitations of Atomic Layer Etching: A Modeling Investigation***, C Huard,* University of Michigan*; Y Zhang, S Sriraman, A Paterson,* Lam Research Corp.*; **Mark Kushner**,* University of Michigan **INVITED**

Atomic layer etching (ALE) techniques are providing several benefits over conventional etching in maintaining critical dimensions, reducing damage and improving selectivity. During conventional etching, simultaneous synergistic reactions between neutral radicals and ions produce continuous etching. Obtaining the benefits of ALE requires sub-cycles separately consisting of self-limiting reactions – typically passivation and etching. In the ideal case, etching results from a synergy between the ALE sub-cycles, with there being no continuous etching due to simultaneous fluxes of radicals and ions during either cycle. In practice, it is difficult to produce conditions that result in this ideal, self-limited reaction sequence.

In this presentation, results will be discussed from a computational investigation of ALE of silicon in Ar/Cl_2 plasmas and SiO_2 in $Ar/C_4F_8/O_2$ plasmas. Reactor scale simulations using the Hybrid Plasma Equipment Model provide the magnitude, energy and angular distributions of reactant fluxes to a wafer. Feature scale modeling was performed using the 3-dimensional Monte-Carlo Feature Profile Model (MCFPM). An important aspect of modeling ALE is representing the finite thickness of the mixing layer formed by ion bombardment. By tracking particles as they penetrate the solid surface, surface mixing and damage are stochastically modeled in the MCFPM.

Investigations were performed of ALE using ideal and non-ideal conditions to determine the possible benefits and limitations of the ALE process. For ideal conditions, aspect ratio dependent etching (ARDE) could be essentially eliminated and surfaces retained their initial smoothness. Introducing continuous etching pathways during ALE of silicon gave rise to ARDE and increased (or introduced) surface roughness. The impact of these non-idealities were investigated in the ability of ALE to clear the poly-silicon gate etch step in 3D finFETs with varying aspect ratios. Results indicate that the ALE process requires less over-etch time than a similar continuous etch, in spite of the non-ideal reaction pathways that result from using realistic reactant fluxes. The impact of reactor scale non-uniformity of fluxes and ion energy distributions was studied for silicon trench etching, demonstrating the limits of flux and energy non-uniformities that can be remediated by the ALE process. The damage induced by ions during over-etch was studied in silicon and SiO_2 when using ALE to clear 3D contacts after a continuous main etch.

Work was supported by Lam Research Corp., DOE Office of Fusion Energy Science and the National Science Foundation.

4:00pm **ALE-SuA-11 ALE TBD 2***, **Nitin Ingle**,* Applied Materials **INVITED**

Please submit your abstract to Della Miller, della@avs.org, immediately for inclusion in the program.

4:30pm **ALE-SuA-13 Significant Improvements of CD Uniformity and ARDE in ODL Mask Etching using a Self-limiting Cyclic Etch Approach***, **Barton Lane**, P Ventzek,* Tokyo Electron America*; A Ranjan, V Rastogi,* TEL Technology Center, America, LLC

Critical dimension global and local uniformity nearing a few atom widths in carbon based hard masks is critical for < 7 nm device fabrication. This is very challenging for continuous and pulsed plasma etch processes. We show that a cyclic etching approach leads to striking improvements in both global and local uniformity. The global uniformity refers to uniformity on the scale length of cm and is typically due to variations in plasma and/or radical densities across the wafer; it is measured by the variation in the critical dimension (CD) and is often termed CD uniformity (CDU). Local uniformity refers to the uniformity between nearby features which have different local geometries for example nested versus isolated features and is often termed aspect ratio dependent etching (ARDE). We consider the etch of a patterned hydrocarbon spin cast film (ODL) using an argon/oxygen chemistry. Such films are used as part of a trilayer mask system and are common in patterning applications. The cyclic scheme breaks the etch into its two fundamental steps: an oxidation step in which oxygen moieties are introduced into the polymer matrix; and a volatilization step in which the oxidized moieties are detached from the polymer matrix. Using pairs of coupons placed in regions of a test bed reactor with significantly different plasma and neutral species densities, we show that using the cyclic scheme relative to a continuous process, that the CDU can be improved significantly. The underlying reasons for the improvement are the self-limiting nature of both the oxidation and the volatilization steps in the etch process. We show by "*in situ* OES SIMS" experiments how this self-limitation process occurs in the case of the argon and oxygen chemistry. In brief, the oxygen containing step leads to an oxidized layer; the argon only sputter step volatilizes this oxidized layer and then rapidly creates a carbonized, hydrogen depleted layer which has a low etch rate following its initial formation. The self-limitation in the argon sputter step is due to the low etch rate of this carbonized layer. In the oxygen step the high density of the carbonized layer prevents the diffusion of oxidizing species into the polymer interior after an initial saturation of the surface with oxidized moieties. This leads to a self-limiting process for a lean chemistry (low oxidizing species density).

4:45pm **ALE-SuA-14 Nanometer-Scale III-V 3D MOSFETs***, **Jesus del Alamo**, W Lu, X Zhao, D Choi, A Vardi,* MIT **INVITED**

In the last few years, as Si electronics faces mounting difficulties to maintain its historical scaling path, transistors based on III-V compound semiconductors have emerged as a credible alternative. To get to this point, fundamental technical problems had to be solved though there are still many challenges that need to be addressed before the first non-Si CMOS technology becomes a reality. Among them, harnessing the outstanding electron transport properties of InGaAs, the leading n-channel material candidate, towards a high-performance nanoscale MOSFET has proven difficult. Introducing a new material system is not the only challenge, scalability to sub-10 nm gate dimensions also demands a new 3D transistor geometry. InGaAs FinFETs, Trigate MOSFETs and Nanowire MOSFETs have all been demonstrated but their performance is still lagging Si. At MIT, we have focused in the last few years in developing etching technology for high aspect ratio III-V fins and nanowire to support the development of sub-10 nm 3D MOSFETs. We have demonstrated fins as narrow as 15 nm with an aspect ratio of ~10 and nanowires with a diameter of 20 nm and an aspect ratio of ~11. Following RIE, our nanowires and fins are trimmed using digital etch. This consists of an oxidation step in O2 plasma and an oxide removal step in a diluted acid. By separating both steps, the process is self-limiting and yields a very precise etching rate (in our case, about ~1 nm/cycle). We have also shown that digital etch improves the sidewall electrical characteristics. Using digital etch, we have been able to demonstrate InGaAs FinFETs with 7 nm wide fins and record transconductance characteristics. Regarding nanowires, the high surface tension of water-based acid makes it impossible to reduce their diameter below ~12 nm. Beyond this dimension, the nanowires collapse due to strong mechanical forces during digital etch and the yield of the process quickly drops to zero. We have recently solved this problem by using alcohol-based acids with a much lower surface tension. Using the same oxidation step, the new technique shows an etch rate of 1 nm/cycle, identical to the conventional approach. Sub-10 nm fins and nanowires with a high yield and mechanical stability have been achieved. InGaAs nanowires with diameter of 5 nm and an aspect ratio > 40 have been demonstrated. The new technique has also been successfully applied to InGaSb-based heterostructures, the first demonstration of digital etch in this material system. Vertical InGaAs nanowire gate-all-around MOSFETs with a subthreshold swing of 70 mV/dec at V_{DS} = 50 mV have been obtained demonstrating the good interfacial quality that the new technique provides.

5:15pm **ALE-SuA-16 Atomic Layer Etch Processes Developed in an ICP/RIE Etching System for Etching III-V Compound Semiconductor Materials***, **Xu Li**, Y Fu, S Peralagu, S Cho, K Floros, D Hemakumara, M Smith,* University of Glasgow, UK*; I Guiney,* University of Cambridge, UK*; D Moran,* University of Glasgow, UK*; C Humphreys,* University of Cambridge, UK*; I Thayne,* University of Glasgow, UK

In this work, we compare several atomic layer etch (ALE) processes developed in an ICP/RIE etching system based on Cl_2/Ar and HBr/Ar chemistries for etching GaN, AlGaN, InAlN, InGaAs, and InGaSb. These processes will be very important in the realisation of various energy efficient electronic devices including gate recess etching of GaN power transistors, and controlled sidewall cleaning in InGaAs and GaInSb finfets and nanowires for continued logic scaling.

Investigations were carried out in an Oxford Instrument PlasmaLab Inductively Coupled Plasma (ICP) etching system with repeat loop function. The etching chemistry is based on the self-limited formation of Al, Ga, In, Sb chlorides or bromides on the semiconductor surface as a consequence of exposure in Cl_2 or HBr gases or plasmas during the sample surface modification step of the ALE cycle. This is followed by an Ar plasma selective surface layer removal step at an optimized RF power level at which the Ar plasma only removes the surface chlorides or bromides. Reducing the power of the Ar plasma process is vital to minimizing damage to the underlying III-V materials.

A parametric exploration of the process space showed that an ALE window can be established for both the Cl_2 and HBr based processes by simply flowing the reactive gas across the sample surface – it is not necessary to establish a plasma of the reactive gases. Further, that given the response time of mass flow controllers on the etch tool, a minimum gas flow time of 2s was required to ensure process stability and repeatability. This relatively long dwell time meant that the reactive gases had to be diluted with Ar – optimal dilution ratios were found to be 8:42 Cl_2:Ar and 6:44 HBr:Ar; all at chamber pressures of 50 mTorr, total gas flow of 50 sccm, and platform temperature of 20°C. Ultimately, processes to produce repeatable removal rates of 0.13 nm/cycle were obtained in this way. Experiments also showed that the Cl_2 and HBr processes modified the III-V surface layers differently, due to the relative volatilities of the chlorine and bromine compounds formed on the III-V material surfaces. The Cl-based chemistry required an Ar plasma RF power of 33 W for surface layer removal, whereas this could be reduced to 20 W for the HBr-based chemistry. This is very important in reducing process induced damage. Experiments showed that there no observable change in either the electron mobility or channel carrier concentration in an AlGaN/GaN HEMT for RF power levels for the Ar plasma of less than 25 W at a chamber pressure of 50 mTorr; therefore an HBr-based ALE process is most appropriate for use in the realization of III-V devices.

5:30pm **ALE-SuA-17 Enhanced Thermal ALE of Aluminum Oxide Combined with ALD for UV Optical Applications***, **John Hennessy**,* Jet Propulsion Laboratory, California Institute of Technology*; C Moore,* University of Colorado - Boulder*; K Balasubramanian, A Jewell,* Jet Propulsion Laboratory, California Institute of Technology*; K France,* University of Colorado - Boulder*; S Nikzad,* Jet Propulsion Laboratory, California Institute of Technology

This work demonstrates the development of a thermal atomic layer etching procedure using alternating exposures of trimethylaluminum and anhydrous hydrogen fluoride that is used to controllably etch aluminum oxide. This ALE process is modified relative to existing HF-based methods through the use of an intermediate reaction during TMA exposure with a conditioning film of lithium fluoride. This is shown to enhance the loss of fluorine surface species and results in conformal layer-by-layer etching of deposited aluminum oxide films. The Al_2O_3 etch rate was measured over a temperature range of 225 to 300 °C, and was observed to increase from 0.8 to 1.2 Å per ALE cycle at a fixed HF exposure. The variation in etch rate is the result of increased surface fluorination during HF exposure, and the extent of this fluorination has a clear dependence on the total effective HF dose delivered per ALE cycle. Nevertheless, the process is shown to be scalable to large area substrates with a post-etch uniformity of better than 2% measured on 125 mm diameter wafers.

This ALE process utilizes the same chemistry previously demonstrated in the ALD of AlF_3 thin films, and can therefore be used to remove the surface oxide from metallic aluminum and replace it with thin fluoride layers in order to improve the performance of ultraviolet aluminum optical components by reducing the loss associated with the oxide layer. We will discuss how this approach has applications in the development of vacuum UV instruments, in next-generation UV mirrors for JPL-NASA astrophysics missions, and in enhancing the performance of nanostructured metallic Al for UV plasmonic applications. The efficacy of the technique is demonstrated by measurements of UV reflectance on evaporated aluminum films undergoing the described ALE + ALD procedure. We will present material characterization by x-ray photoelectron spectroscopy, ellipsometry, and atomic force microscopy; and we will discuss the mechanism associated with the etch enhancement produced by co-reaction with LiF.

Atomic Layer Etching
Room Plaza D - Session ALE-MoM

Atomic Layer Etching Session III (8:00-10:00 am) and Session IV (10:45 am-12:00 pm)

Moderators: Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, Sumit Agarwal, Colorado School of Mines

8:00am **ALE-MoM-1 Selectivity in Thermal Atomic Layer Etching*,* *Younghee Lee*,** *S George,* University of Colorado **INVITED**

Selectivity in etching is required to remove one material in the presence of other different materials. Selectivity in atomic layer etching (ALE) is important for advanced semiconductor fabrication. Selective ALE, together with selective atomic layer deposition (ALD), could lead to the maskless fabrication of device structures. This talk will examine the selectivity of thermal ALE by exploring the etching of a number of important semiconductor materials including Al_2O_3, HfO_2, ZrO_2, SiO_2, Si_3N_4, and TiN. The thermal ALE will be conducted using various sequential, self-limiting reactions.

The first part of the talk will examine selective thermal ALE based on fluorination and ligand-exchange reactions.[1] Fluorination is achieved using HF as the fluorine reactant. Different metal precursors provide various ligands that may transfer during ligand-exchange. Etching occurs when the transferred ligands produce stable and volatile metal products that may leave the surface. The metal precursors are tin(II) acetylacetonate ($Sn(acac)_2$), trimethylaluminum (TMA), dimethylaluminum chloride, and $SiCl_4$.[2] These metal precursors provide acac, methyl, and chloride ligands for ligand exchange. Spectroscopic ellipsometry was used to measure the etch rates.

The spectroscopic ellipsometry measurements revealed that HfO_2 was etched by all of the metal precursors. Al_2O_3 was etched by all of the metal precursors except $SiCl_4$. ZrO_2 was etched by all of the metal precursors except TMA. In contrast, SiO_2, Si_3N_4, and TiN were not etched by any of these metal precursors. These results can be explained by the stability and volatility of the possible etch products. Temperature can also be used to obtain selective thermal ALE. The combination of different metal precursors with various ligands and different temperatures can provide multiple pathways for selective thermal ALE.

The second part of this talk will present results for the thermal ALE of TiN using a new etching mechanism. Spectroscopic ellipsometry and x-ray reflectivity analysis showed that the TiN films were etched linearly versus the number of ALE cycles. In contrast, this new method was highly selective and did not etch Al_2O_3, HfO_2, ZrO_2, SiO_2, and Si_3N_4. The etch rates for TiN ALE increased with temperature from 0.06 Å/cycle at 150 °C to 0.20 Å/cycle at 250 °C and stayed nearly constant for temperatures ≥250 °C. The thermal ALE of many other materials should be possible using this new etching mechanism.

[1] Younghee Lee and Steven M. George, *ACS Nano* **2015**, 9, 2061.

[2] Younghee Lee, Craig Huffman, and Steven M. George, *Chemistry of Materials* **2016**, 28, 7657.

8:30am **ALE-MoM-3 Modeling the Chemical Mechanism of Thermal ALE of Alumina by HF and Tin Acetylacetonate*,* *Simon Elliott*,** Tyndall National Institute, University College Cork, Ireland

Lee and George have established a new platform for the conformal removal of oxide materials with atomic-level control, termed 'thermal atomic layer etch' (ALE) [1]. By-products, intermediates and limiting factors have been deduced from in situ infrared spectoscopy and quartz crystal microbalance measurements [2]. In this study, we use density functional theory (DFT) to further investigate the mechanism of thermal ALE. We focus on the etching of Al_2O_3 by HF and $Sn(acac)_2$ [acac=acetylacetonate], and also consider the viability of alternative reagents and substrates.

By simulating the interaction of HF with an alumina surface, we confirm that H2O is the by-product and that this apparently self-limiting reaction fixes the maximum etch rate that can be achieved. We find that other halides HCl, HBr and HI are also reactive in this part of the ALE cycle.

Further calculations reveal that the ligand-exchange reactions of the Sn $(acac)_2$ co-reagent with a fluorinated surface require thermal activation. A range of by-products are possible. However, brominated and iodated surfaces are inert towards this co-reagent.

The study is extended to screening other substrates by computing the thermodynamics of the overall etch reaction. The computed data show that etching of HfO_2 and ZrO_2 with HF+$Sn(acac)_2$ is more favourable than etching Al_2O_3. The fact that the experimental ALE rate of HfO_2 and ZrO_2 is lower than that of Al_2O_3 [3] emphasises the need to consider not just thermodynamics, but also how kinetics affects residual coverages and hence etch rates during the ALE cycle.

[1] Y. Lee, J. W. DuMont & S. M. George, ECS J. Solid State Sci. Techn. 4, N5013 (2015); S. M. George & Y. Lee, ACS Nano 10, 4889 (2016).

[2] Y. Lee, J. W. DuMont & S. M. George, Chem. Mater. 27, 3648 (2015).

[3] Y. Lee, C. Huffman & S. M. George, Chem. Mater. 28 7657 (2016).

8:45am **ALE-MoM-4 Integrating Atomic Layer Deposition and Etching to Achieve Selective Growth*,* *Stacey F. Bent*,** Stanford University **INVITED**

A variety of steps in electronic device fabrication may benefit from selective processing, including those in both the front end and back end of line. Area selective atomic layer deposition (ALD), an approach in which deposition occurs on specific regions of a substrate (active) while other regions (passive) remain free of deposition, has received much attention over the past decade. However, area selective ALD processes typically break down after more than a few nanometers of material is deposited, degrading the selectivity between active and passive regions of the substrate. We have found that combining area selective ALD with chemically-selective etching can significantly enhance selective processing. We introduce a process in which self-assembled monolayers (SAMs) are used to create passive regions of a surface, allowing ALD to preferentially deposit on the remaining active areas. Imperfect selectivity results, however, because the ALD process begins to nucleate on the regions of the surface covered with the SAM. Selectivity is regained when the area selective ALD is combined with selective removal of any residual dielectric film with a mild etchant. Selective growth of more than 60 nm of metal oxide dielectric material has been achieved using this combined deposition/etching process. Strategies to expand this process to cycle between deposition and etching, and to eliminate the SAM, will be discussed.

9:15am **ALE-MoM-6 ALE and ALC: Computational Assessment of Opportunities and Challenges in Nanoelectronic Applications*,* *Sumeet C. Pandey*,** Micron **INVITED**

Realization of atomic-scale control during processing can catalyze incorporation of ultra-thin materials (low-dimensional) with device functionality on complex three-dimensional topographies. Atomic layer etching and cleans have been cited as potential processes that can help enable a sustainable semiconductor technology roadmap, however, there is a clear need to identify paths to achieving applications in high-density semiconductor manufacturing. We will leverage the literature data and learning from ALD community to evaluate thermal ALE regime against various options for precursor chemistry, process parameters, and feature aspect ratios. The talk will discuss findings relevant to nanoelectronic applications with emphasis on the surface reactions and its control through process conditions and chemistry using first-principles-based multiscale modeling.

9:45am **ALE-MoM-8 Reactor Scale Uniformity Enabled by Atomic Layer Etching*,* *Chad Huard*,** *S Lanham, M Kushner,* University of Michigan

One of the possible benefits of atomic layer etching (ALE) is improved uniformity at the wafer scale when compared to continuous etching processes. The ability to produce uniform etch rates in spite of non-uniform reactant fluxes stems from the self-limited nature of the reactions used for ALE. Similar to atomic layer deposition (ALD), utilizing self-limited reactions enables step times to be extended until surface coverage is complete and uniform for each of the ALE sub-cycles. Wafer scale non-uniformities in the incoming fluxes therefore should not, in principle, translate into non-uniformities in etch rates. While ideally self-limited reactions in ALE are expected to produce perfectly uniform etch profiles across the wafer, it is not clear what effect the presence of non-self-limited reactions – which are inevitable in conventional plasma equipment – will have on the wafer scale uniformity.

ALE using non-uniform and non-ideal fluxes was computationally investigated using the 3-dimensional Monte-Carlo Feature Profile Model (MCFPM). The etching of silicon trenches was used as an example case. The ALE of silicon was accomplished using a Cl_2 plasma to passivate the surface, and an Ar plasma (with a small RF bias) to remove the passivated layer, while continuous etching was simulated using an Ar/Cl_2 mixture with similar ion energies. The Hybrid Plasma Equipment Model was used to simulate fluxes, energy and angular distributions as a function of radial position on the wafer in an inductively coupled plasma (ICP) reactor. By changing the position of the ICP antenna, the uniformity of reactant fluxes to the wafer was varied.

The simulated etch profiles indicate that changes in the ion flux to the wafer produce a nearly linear change in etch rate for the continuous etching cases, while when operating in ALE mode, there was a much smaller dependence of etch rate on the incoming ion flux. The ability of the ALE process to tolerate non-uniform fluxes is not only dependent on the lack of continuous etching mechanisms (high ALE synergy), but it requires that the system is operated in a regime where a large proportion of the incoming reactant fluxes are rejected by the saturated surfaces. For sub-saturated conditions, the ALE etch rate is also linearly dependent on ion flux, despite having little or no continuous etching.

Work supported by LAM Research Corp., the DOE Office of Fusion Energy Science and the National Science Foundation.

10:45am **ALE-MoM-12 Thermal Atomic Layer Etching of Cobalt Metal Films***, **Charles H. Winter**, W Waduge,* Wayne State University **INVITED**

Atomic layer deposition (ALD) produces films with sub-nanometer thickness control and perfect conformality because of the inherent self-limited growth mechanism.[1] The opposite of ALD is atomic layer etching (ALE), where films are etched with a layer-by-layer, self-limited mechanism.[2] To date, ALE has been mostly focused on plasma-based processes.[2] However, plasma ALE requires expensive equipment and the energetic plasma ions can damage substrates, films, and equipment. Accordingly, there is an urgent need to develop <u>thermal</u> ALE processes, which use carefully designed, exothermic chemical reactions to achieve etching. The first thermal ALE processes were only reported in 2015 for Al_2O_3,[3] AlF_3,[4] and HfO_2[5] films. Cobalt metal films are widely used to encapsulate copper in microelectronics devices to stop the electromigration of copper.[6] The thermal ALE of cobalt metal would be valuable for the manipulation of cobalt liners and caps, however, the thermal ALE of cobalt metal films has not been reported. Herein, we will describe a thermal ALE process for cobalt metal, which entails treatment of 50 to 100-nm thick cobalt metal films with formic acid, followed by the organic ligand $Me_2NNHC(O)tBu$ (L^1H). The etch rate is about 0.08-0.10 Å /cycle at 180 ° C. Presumably, the formic acid pulses oxidize the surface cobalt atoms to cobalt(II) formate, and then the L^1H pulse reacts with the cobalt(II) formate to afford $Co(L^1)_2$. We recently reported the synthesis and structure of $Co(L^1)_2$, and found that it sublimes at 75 °C/0.05 Torr and undergoes solid state thermal decomposition at 245 °C.[7] Accordingly, $Co(L^1)_2$ should be evolved as a volatile species under the ALE conditions. Additional details of the ALE process will be presented.

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2. K.J. Kanarik, T. Lill, E.A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, R.A. Gottscho, J. Vac. Sci. Technol. A 33 (2015) 020802.

3. Y. Lee, S.M. George, ACS Nano 9 (2015)2061-2070. Y. Lee, J.W. DuMont, S.M. George, Chem. Mater. 27 (2015)3648-3657.

4. Y. Lee, J.W. DuMont, S.M. George, J. Phys. Chem. C 119 (2015) 25385-25393.

5. Y. Lee, J.W. DuMont, S.M. George, ECS J. Solid St. Sci. Technol. 4 (2015) N5013-N5022.

6. C.-C. Yang, P. Flaitz, P. Wang, F. Chen, D. Edelstein, IEEE Electron Dev. Lett. 31 (2010) 728-730.

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11:15am **ALE-MoM-14 WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Etching Mechanisms***, **Nicholas Johnson**, S George,* University of Colorado

Atomic layer etching (ALE) of metals is important for the controlled removal of many valuable semiconductor materials such as conductors (e.g. W, Cu), metal gates (e.g. Ta, Ti) and metals in magnetic multilayers (e.g. Co, Fe). However, few reports exist for metal ALE using either plasma or thermal processes. Conventional thermal ALE that has defined recent work on metal oxide [1] and metal nitride [2] materials does not work for metals. New reaction pathways are required to etch metals. This study targets W ALE and examines both WO_3 ALE and W ALE as W oxidation to WO_3 is needed to define self-limiting reactions for W ALE.

WO_3 ALE was demonstrated using an AB exposure sequence with boron trichloride (BCl_3) and hydrogen fluoride (HF). BCl_3 and HF etch WO_3 by a "conversion-fluorination" mechanism. The BCl_3 converts the WO_3 surface to a B_2O_3 layer while forming volatile WO_xCl_y. HF then spontaneously etches the B_2O_3 layer producing volatile BF_3 and H_2O products. WO_3 films were formed by oxidizing W ALD films with an oxygen plasma at 280^{o}C. *In situ* spectroscopic ellipsometry (SE) studies determined that the BCl_3 and HF reactions were self-limiting versus exposure. WO_3 ALE etch rates increased with temperature from 0.55 Å/cycle at 128°C to 4.19 Å/cycle at 207°C. W served as an etch stop because BCl_3 and HF could not etch the underlying W film.

W ALE was performed using a three-step "oxidation-conversion-fluorination" mechanism. This is an ABC exposure sequence that where the W surface is first oxidized to a WO_3 layer and then the WO_3 layer is etched with BCl_3 and HF. SE could simultaneously monitor the W and WO_3 thicknesses and conversion of W to WO_3. Oxidation of the W surface was performed using either O_2 plasma or O_3. SE measurements showed that the W film thickness decreased linearly with number of ABC reaction cycles. The etch rates for W ALE were between 1.2-1.6 Å/cycle at 207°C depending on oxidation reactant and reaction conditions. In contrast, the WO_3 thickness was variable and could either increase or decrease depending on the oxidation conditions.

[1] Younghee Lee, et al., "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994-3003 (2016).

[2] Nicholas R. Johnson, et al., "Thermal Atomic Layer Etching of Crystalline Aluminum Nitride Using Sequential, Self-Limiting HF and $Sn(acac)_2$ Reactions and Enhancement by H_2 and Ar Plasmas", *J. Vac. Sci. Technol. A* **34**, 050603 (2016).

11:30am **ALE-MoM-15 Plasma-Enhanced Atomic Layer Etching of TiN and TaN with Organic Masks***, **Nathan Marchack**, J Papalia, R Bruce, S Engelmann, E Joseph,* IBM TJ Watson Research Center **INVITED**

The concept of atomic layer etching (ALE) has garnered significant interest for future technology node patterning applications, owing to its potential for unparalleled control over the vertical dimensions of subtractive etching as well as minimal damage through a set of self-limiting reactions.[1] The continual downscaling of feature sizes and integration of novel materials has already begun to be limited by the complex nature of conventional continuous-wave plasmas, in which etch and deposition reactions occur simultaneously and cannot be fully decoupled from the variation of physical parameters such as power, pressure and gas flows. The ability of ALE to at least partially delineate these competing mechanisms in a plasma could be a powerful tool to overcoming these challenges.

This talk focuses on the plasma-enhanced ALE of TaN and TiN, which often serve as hardmasks for patterning of etch-resistant metals for non-volatile memory applications. These materials also function as the top electrode in memory cells due to their conductive nature, so the ability to generate patterns with low damage at tight pitches becomes increasingly important for future device technology. A plasma-enhanced atomic layer etch (PE-ALE) process utilizing sequential cycles of Cl_2 (deposition) and He/H_2 (etch) chemistries separated by purge steps was used to pattern TiN and TaN lines using an OPL mask at 100nm CD and 200nm pitch. Compared to a continuous wave Cl_2 plasma, the PE-ALE process demonstrated virtually no metal residue on the OPL mask and SiOx stop layer; as well as a powerful knob for tuning the profile and CD of the features by controlling the purge times between cycles.

[1] G. S. Oehrlein, D. Metzler, and C. Li, Atomic Layer Etching at the Tipping Point: An Overview

ECS J. Solid State Sci. Technol. 2015 4(6): N5041-N5053

Atomic Layer Etching
Room Plaza D - Session ALE+AF-MoA

Atomic Layer Etching Session V (1:30-3:30 pm)/ALD Fundamentals: Process Development (4:00-5:45 pm)

Moderator: Mike Cooke, Oxford Instruments Plasma Technology

1:30pm **ALE+AF-MoA-1 *In situ* Spectroscopic Methods for Atomic Layer Etching and Atomic Layer Deposition*, Yves Chabal,*** *J Klesko, A Dangerfield, J Veyan,* University of Texas at Dallas **INVITED**

As a relatively new technique, Atomic Layer Etching requires a fundamental understanding of the surface chemical processes that govern its operation. Most reported ALE processes are based on halogenation reactions followed by ion or noble gas atom bombardment, but there have recently been promising thermal ALE developments based on sequential fluorination and ligand exchange reactions. In all cases, knowledge of the fluorinated surface species and resulting surface composition after bombardment or exchange reactions is helpful to derive a mechanistic understanding of the surfaces. Such knowledge requires *in situ* characterization, in particular chemical bonding information that can be derived from vibrational spectroscopy.

We have developed reactors that can be used both for ALD and ALE, in which *in situ* IR spectroscopy is performed either in transmission for semiconductor substrates or reflection for metaling substrates, to examine gas phase or plasma-induced processes. We have also developed an ultra-high vacuum cluster tool in which IR spectroscopy, X-ray photoemission and Low Energy Ion Scattering can be performed on substrate subjected either to gas phase exposures or plasma treatment (remote plasma). Examples will be presented, taken mostly from ALD studies, which illustrate how mechanistic information can be derived from *in situ* IR spectroscopy, including the interaction of plasmas with oxides, nitrides and metal alloy films and the role of TMA in either stabilizing interfaces or enhancing surface reactions in ALD processes.

A schematic drawing of UHV cluster tool with in situ IR spectroscopy, XPS and LEIS is shown below.

2:00pm **ALE+AF-MoA-3 An *in situ* Optical Diagnostic Study of the Process Conditions that Affect the Etch per Cycle in ALE of SiO_2***, S Agarwal,* ***Ryan Gasvoda,*** *N Leick,* Colorado School of Mines*; A van de Steeg,* Eindhoven University of Technology, Netherlands*; R Ovanesyan, J Klein,* Colorado School of Mines*; R Bhowmick, E Hudson,* Lam Research Corp.

With the advent of 3-D architectures in semiconductor devices combined with shrinking device dimensions, precise patterning requirements pose new challenges for conventional plasma etching. One recently proposed technique to address the limitations of continuous plasma etching is atomic layer etching (ALE), which can simultaneously enable directional control, etch selectivity, and atomic-level removal rates. ALE has been extensively studied for a variety of materials including Al_2O_3, HfO_2, Si, and silicon-based dielectrics. In this study, we have explored the atomistic-level details of an ALE process for SiO_2 based on a CF_x deposition step using a C_4F_8/Ar plasma, which is followed by an ion-assisted Ar plasma activation step to release the fluorine in the CF_x film for SiO_2 etching.

Specifically, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE of SiO_2 to monitor the surface composition, and the net SiO_2 and CF_x film thickness, respectively. Infrared spectra recorded after the CF_x deposition half-cycle (spectrum in blue in Fig. 1) predominantly shows an increase in CF_x ($x = 1, 2, 3$) stretching vibrations at ~1230 cm^{-1}, but it also shows very weak C-O-Si and SiF_x ($x = 1, 2, 3$) stretching vibrations at ~1110 and ~970 – 1000 cm^{-1}, respectively. Given that the latter two vibrational bands appear as weak features, this indicate that a very thin mixing layer is formed at the SiO_2-CF_x interface compared to continuous etching of SiO_2.

After exposing the CF_x film on SiO_2 to an Ar plasma for 10 s, the spectrum in dark green in Fig. 1 clearly shows the simultaneous removal of SiO_2 and CF_x during Ar^+ activation. Further exposure to Ar plasma continues the etch of SiO_2 until the CF_x layer is completely removed as seen in the next four spectra. The last 10 s of Ar plasma exposure (red spectrum in Fig. 1) shows continued SiO_2 etching even after the removal of CF_x layer, which indicates that there is an additional source of etchant in the reactor. Sequential ALE cycles also show an increase in the etch per cycle as a function of cycle number (Fig. 2). This increase occurs even though the infrared spectra confirm that the deposition step remains reproducible from cycle to cycle as also seen in the inset in Fig. 2. Therefore, the increase in the etch per cycle occurs due to the Arplasma half-cycle as Ar^+ liberate CF_x radicals from the reactor walls that participate in the etching process. This chamber wall effect manifests as an increase in the etch per cycle since CF_x film accumulates on the chamber walls and, therefore, more F is available for etching in later cycles.

2:15pm **ALE+AF-MoA-4 New Innovative Etching Approaches for Future Generation by Controlling the Surface Reaction at Atomic-Level*, Masanobu Honda,*** *T Katsunuma,* Tokyo Electron Miyagi Ltd., Japan **INVITED**

A new technology has been developed using the Atomic Layer Etching (ALE) and Atomic Layer Deposition (ALD) concepts. It has been applied to self-aligned contacts (SAC) and patterning processes, for the sub 7nm technology generation.

In the SAC process, ultra-high selectivity of SiO_2 etching towards SiN is required, for which we have developed Quasi-ALE technique for SiO_2 etching. We were able to significantly improve the trade-off between the etching ability of SiO_2 on the micro slit portions and SiN selectivity. Quasi-ALE precisely controls the reaction layer thickness of the surface, by controlling the radical flux and ion flux independently, and hence enables etching at lower ion energies.

On the other hand, in the patterning processes, the shrinking of critical dimensions (CD) without loading is mandatory. Therefore, we developed a new process flow that combines ALD technique and etching. With this method, we were able to achieve CD shrinking at atomic-layer level precision for various patterns, without causing CD loading. In addition, we were also able to uniformly control the CD shrinkage amount across the whole wafer. This is because this technique takes advantage of the deposition step which is independent of the pattern density and the location on the wafer by self-limited reactions.

As discussed earlier, the fine processing technology will become more important for future generation. In recent years, to meet the highly complex requirements imposed by device fabrication processes, alternative process was developed for thin layer etching [1]. We have made several improvements on this new approach and applied it to various etching processes [2]. In the presentation, the newly improved approach will also be introduced in addition to Quasi-ALE and CD shrinking technique without causing CD loading.

1. N Posseme, O Pollet and S Barnola 2014 Alternative process for thin layer etching: Application to nitride spacer etching stopping on silicon germanium Applied Physics Letters105 051605

2. Sonam D Sherpa and Alok Ranjan 2017 Quasi-atomic layer etching of silicon nitride J. Vac. Sci. Technol. A 35 01A102

2:45pm **ALE+AF-MoA-6 Controlled Layer-by-Layer Etching of ALD Grown Ta_2O_5 Thin Films*, Anil Mane,*** *J Elam,* Argonne National Laboratory

Precisely controlled layer-by-layer etching processes for metal oxide films are required to enable the fabrication of 3D-microelectronic devices such as semiconductor memories, logic, and MEMS. Ta_2O_5 is a high-k dielectric and is useful in flash memory as well as resistive random access memory (RRAM) devices. Here we developed a precisely controlled layer-by-layer etching process for Ta_2O_5 thin films using alternating exposures to MoF_6 and H_2O vapors. For example, etching of ALD Ta_2O_5 thin films deposited using either $TaCl_5$ or TaF_5 and H_2O can be perform in either a one-step, chemical vapor etching manner (CVEt) or in a layer-by-layer self-limiting controlled manner (ALEt). We used in-situ quartz crystal microbalance (QCM) measurements to monitor the deposition and etching of the Ta_2O_5 layers (Figure 1). Next, the etched Ta_2O_5 thin films were analyzed by spectroscopic ellipsometry to determine the thickness and refractive index. These ex-situ measurements confirmed the findings from our in-situ QCM studies. Here we will discuss the details of the self-limiting ALD growth and etching of Ta_2O_5 Thin films.

3:00pm **ALE+AF-MoA-7 Atomic Layer Etching Mechanism of 2D MoS_2 Layers*, Ki Seok Kim,*** *K Kim, Y Ji, G Yeom,* Sung Kyun Kwan University, Republic of Korea

The single MoS_2 monolayer has a $S_{(top)}$-Mo-$S_{(bottom)}$ crystal structure that is consisted of a three-atom-thick covalent bonds between Mo and S atoms; thereby, the ALE mechanism using Cl as the adsorption species and Ar^+-ion as the desorption species can be quite different from other two-dimensional (2-D) materials with one-atom-thick materials such as graphene. We have investigated that the MoS_2 ALE mechanism from bilayer MoS_2 to monolayer MoS_2 using controlled Cl radical adsorption and Ar^+-ion desorption as a function of Ar^+-ion desorption time with a monoenergetic Ar^+-ion energy of 20 eV. The result showed that Cl atoms are adsorbed on top S atoms and trapped between top S atoms and Mo atoms by van der Waals force during the Cl radical adsorption. The reults also showed that the monolayer MoS_2 is sequentially removed from the top S atoms by S-Cl, Mo by Mo-Cl, and bottom S atoms by selective sputtering. XPS data showed no change of chemical composition and no structural damage on the exposed 2nd MoS_2 layer after one-cycle ALE. In addition, the MoS_2 FET fabricated with the monolayer MoS_2 obtained after the one-cycle MoS_2 ALE of a bilayer MoS_2 exhibited the similar electrical charteristics as those fabricated with a pristine monolayer MoS_2, therefore, nearly no electrical damage on the MoS_2 layer was ocurred by the MoS_2 ALE process. It is believed that the ALE technique used in the experiment can be applicable to all the layered TMD materials including MoS_2 for next generation nano-devices.

3:15pm **ALE+AF-MoA-8 ALD & Quasi-ALE Patterning Application in EUV Contact Etch***, **Hongyun Cottle**, D O'Meara, A Metz,* Tokyo Electron Limited*; P Biolsi,* TEL Technology Center, America, LLC*; S Nakamura, T Yang,* Tokyo Electron Limited*; M Honda,* Tokyo Electron Miyagi Ltd., Japan*; S Morikita,* Tokyo Electron Limited

Continued pitch scaling of semiconductor devices to 7nm node and beyond utilizing conventional 193i based multiple patterning techniques is rapidly driving up cost, complexity, and variability control. EUV patterning can be used to mitigate or delay the challenges of pitch scaling through multiple patterning, but introduces new challenges of its own. EUV lithography introduces new types of resists that are thinner and less etch resistant compared to conventional 193nm resists. Interactions of polymers with plasma etch environments can lead to large changes of the polymer material properties and the three-dimensional nanostructures they pattern. Mask deformation during such etch process can lead to changes in nanoscale topography of device features, often with undesirable consequences, such as increased LER and LWR, tip-to-tip degradation, and line wiggling. Plasma etch faces a significant challenge to optimize its process window to enable high yields with EUV patterning.

This paper presents the synergetic combination of ALD & Q-ALE in EUV contact mask etch to overcome the above-mentioned EUV lithography changelings. ALD application at mask open level improves incoming LWR/LER and defines what can be transferred to final etch product. Q-ALE mask open improves EUV photoresist etch selectivity by greater than three-fold while maintaining critical feature dimensions, such as elliptical contact minor vs major axis CD ratio. By utilizing a direct current superposition (DCS) technology, EUV photoresist can also be treated to improve not only its etch resistant, but also LER and LWR. These unique processes (ALD vs. Q-ALE vs. DCS) can be applied independently or in combination utilizing Tokyo Electron advanced etchers. Through their accumulative effects, these processes offer a wide range of etch capabilities to enable EUV lithography to 7nm and beyond.

Reported is the structural characterization pre and post-etch detailing LER and LWR improvement, and shrink ratio control. In addition, a mechanistic model will be proposed based on thin film compositional analysis and process trend data.

4:00pm **ALE+AF-MoA-11 Boron Nitride Growth at Room Temperature Using Electron Enhanced Atomic Layer Deposition (EE-ALD)***, **Jaclyn Sprenger**, H Sun, A Cavanagh, S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) can drastically reduce the temperatures required for film growth. This temperature reduction occurs because electrons can desorb surface species by electron stimulated desorption (ESD) to create very reactive "dangling bonds". Precursors can then adsorb efficiently on the dangling bonds. EE-ALD lowers the thermal budget and enables the deposition of thin films on thermally sensitive substrates. EE-ALD has been demonstrated previously for the deposition of polycrystalline GaN [1] and amorphous Si [2] at room temperature.

BN film growth by EE-ALD was performed at room temperature on Si (111) substrates using alternating doses of borazine ($B_3N_3H_6$) and low-energy electrons. Borazine is a single-source precursor for BN deposition. *In situ* ellipsometry was performed during the BN EE-ALD. These ellipsometry measurements yielded a linear growth rate of ~0.45 Å/cycle for electron energies of 100 eV with an electron current of 100 μA for 60 s. This *in situ* growth rate was confirmed by *ex situ* spectroscopic ellipsometry. A BN film with a thickness of 90 nm was deposited after 2000 EE-ALD cycles (see supplemental Figure 1).

Film composition was studied with *ex situ* XPS (see supplemental Figure 2). The BN composition is consistent throughout the film with a B/N ratio of 1.3/1. The films are pure with C and O concentrations of only <3 at.% in the bulk of the film. A thin, self-passivating surface oxide resulting from atmospheric exposure is present. In addition, *ex situ* FTIR transmission was performed on the BN films. These FTIR measurements yielded an absorption peak at ~1370 cm^{-1} that is consistent with hexagonal BN.

Doubling the electron emission current used for BN film growth from 100 μA to 200 μA with exposure times of 60 s yielded slightly lower film growth rates. However, these films had a higher measured index of refraction. This suggests that an electron current of 100 μA may be sufficient to remove all the surface hydrogen in the electron beam. The fairly flat BN thickness spatial profiles are also consistent with self-limiting hydrogen desorption. The higher electron current of 200 μA for 60 s does appear to increase the film density.

[1] J.K. Sprenger, A.S. Cavanagh, H. Sun, K.J. Wahl, A. Roshko and S.M. George, "Electron Enhanced Growth of Crystalline Gallium Nitride Thin Films at Room Temperature and 100°C Using Sequential Surface Reactions", *Chem. Mater.* **28**, 5282 (2016).

[2] J.K. Sprenger, A.S. Cavanagh, H. Sun and S.M. George, "Electron Enhanced Atomic Layer Deposition (EE-ALD) of Silicon Films at Room Temperature", Presentation at ALD2016 in Dublin, Ireland.

4:15pm **ALE+AF-MoA-12 Catalyzed Atomic Layer Deposition of Silicon Oxide at Ultra-low Temperature using Alkylamines***, **Tirta Rona Mayangsari**, J Park, L Yusup, J Gu,* Sejong University, Republic of Korea*; J Yoo, H Kim,* JUSUNG Engineering, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

The dielectric spacer in multipatterning process such as self-aligned double patterning (SADP) or self-aligned quadruple patterning (SAQP) has been adopted to increase the density of line pattern with only single exposure. Deposition of the dielectric spacer directly on the photoresist patterns instead of the hardmask patterns would reduce several process steps. For this purpose, ultra-low temperature deposition of the spacer film is highly required to avoid the distortion of the underlaying photoresist patterns. Atomic layer deposition (ALD) processes of SiO_2 dielectric thin film at ultra-low temperature have been studied by using pyridine catalyst [1] or O_2 plasma [2]. Catalyzed ALD of SiO_2 is especially suitable for the cost-effective SADP or SAQP process flow, because it can avoid the damages of the underlying photoresist patterns by O_2 plasma. However, in the catalyzed ALD process using pyridine, the generation of salts is still an issue as a result of reaction between the catalyst and ALD reaction byproducts, HCl [3]. To resolve this issue, catalyst having less reactivity with HCl is needed. In the present study, we simulated the reaction of various catalysts with HCl as well as the interaction between catalysts and precursors by density functional theory (DFT) calculation.

Lewis-base amine catalysts with different alkyl ligand and hydrogen concentration were studied, and silicon chlorides with different numbers of silicon and chlorine atoms were investigated. The length and the energy of hydrogen bond between catalyst and water molecule were calculated for each catalysts to expect the catalytic activity, and the energies of the formation and desorption of the catalyst-HCl salt were also calculated. The effects of molecular structures of catalysts and silicon precursors on the catalytic activity and the salt formation were confirmed by in-situ FTIR analysis. Finally, the growth rate, the chemical composition, and the step coverage of the deposited films were analyzed for different combinations of catalyst and silicon precursor.

[1] J.W. Klaus et al, Science, 287 (1997) 1934.

[2] G. Dingemans et al, ECS Transactions, 35 (2011) 191.

[3] Y. Du et al, J. Phys. Chem. C, 111 (2007) 219.

4:30pm **ALE+AF-MoA-13 Low Resistance ALD TiN from Low Temperature Thermal N_2H_4 + $TiCl_4$***, **Steven Wolf**, M Kavrik, J Park,* University of California San Diego*; R Holmes, D Alvarez, J Spiegelman,* RASIRC*; A Kummel,* University of California San Diego

Titanium nitride (TiN) has been extensively studied in semiconductor devices because of its ideal thermal, mechanical, and electrical properties and its ability to act as a metal diffusion barrier [1]. ALD TiN has previously been performed using a wide range of Ti precursors including halides (i.e. TiI_4, $TiCl_4$) and metal organics (i.e. TDMAT, TEMAT), as well as nitrogen sources (thermal/plasma NH_3, N_2/H_2, etc). Metal halide precursors are preferred over metal organic grown films that typically contain high levels of carbon and oxygen contamination; this contamination has been correlated with an increase in TiN film resistivity [2]. Plasma enhanced-ALD TiN has been shown to achieve optimal growth rates with lower contamination at temperatures below 350°C, but the film and underlying substrate can suffer from plasma induced damaged [1,3]. In this study, low temperature thermal ALD TiN from anhydrous N_2H_4 and $TiCl_4$ was performed on a SiO_xN_y substrate, and the deposited films were studied using x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and atomic force microscopy (AFM). In addition, the resistivity of thin TiN films was measured using a modified four-point probe measurement, in which 30nm thick Ni dots with 150µm diameter and 250µm spacing were deposited on top of ALD TiN films.

SiO_xN_y substrates underwent an ex-situ degrease procedure with acetone, methanol and water before being loaded into vacuum. A 275°C UHV anneal was performed to remove surface hydrocarbon. Subsequent cycles of TiN ALD at temperatures between 275°C and 350°C were performed resulting in an estimated 3nm thick film with a Ti/N ratio of ~3/4 with chlorine comprising ~10% in the normalized XPS spectrum. Uniform deposition with subnanometer RMS roughness was seen from STM and AFM measurements. After depositing Ni dots and performing a modified four-point probe measurement, film resistivity was estimated at ~176 µΩ-cm. In conclusion, the thermal low-temperature TiN ALD using anhydrous N_2H_4 and $TiCl_4$ was performed and the subsequent low impurity TiN film's chemical, topographical and electrical properties were characterized.

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4:45pm **ALE+AF-MoA-14 Study of the Isotropic Behavior of AZO Conductivity Deposited by Atomic Layer Deposition - Effect of Film Thickness**

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Keywords: ALD, TCO, transparent electrode, OLED, anisotropic conductivity

Al-doped ZnO (AZO) is one of the most recently studied Transparent Conductive Oxides (TCO), especially because of its numerous attractive properties as electrode in OLED, OPV or OTFT. Atomic Layer Deposition (ALD) allows a precise control of AZO performances versus deposition temperature, doping ratio and thickness. Conventional AZO measurements using four-point probe setup or Hall effect (fig 1 a) are mainly representative of the combination of vertical and lateral conductivity of the film. However, when those TCO have to be integrated into an OLED stack as transparent electrode, carrier injection is made in the vertical direction (fig 1 b). We believed that AZO is an anisotropic material, particularly because of its growth as nanolaminate, i.e. alternating ZnO bulk layers with Al_xO_y interlayers in ALD mode.

In this work, we want to study the anisotropy of the electrical conductivity of AZO films, as depicted in figure 1 a and 1 b. Furthermore, as the AZO film thickness impacts the electro-optical characteristics, its influence on the vertical conductivity needs to be highlighted.

We firstly investigated the major differences between very thin films (approximately 10 nm), and thicker AZO (60 nm, 110 nm) deposited on 200 mm silicon and silicon oxide wafers, respecting exactly the same growth conditions. The resistivity decreases from ~ 100 mΩ.cm for very thin films to 3 mΩ.cm when the thickness is increased above a hundred of nanometers. Identical variations have been measured for the square resistance and are consistent with other studies [1]. These trends are known and can be attributed to the growth parameters like preferential orientation, nucleation delay and ionized impurities scattering [2, 3].

In a second step, the same AZO recipes were deposited onto structured TiN layers, where the TCO films can be evaluated in the OLED configuration, as an anode (fig 1 b). In order to correlate the AZO behavior in both configurations and function of the deposited thicknesses, attention will be carried out on crystalline profile using XRD measurements and onto electro-optical characteristics of the OLED.

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5:00pm **ALE+AF-MoA-15 Growth Behaviour and Stability of Atomic Layer Deposited MoO_3 by $Mo(CO)_6$ and H_2O/O_3 Precursors**

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Molybdenum trioxide has been shown to be a lucrative material e.g., for catalysis [1] and electrochromic applications [2]. This applicability can be credited to the multitude of oxidation states and polymorphs of the compound. Despite MoO_3 complex chemistry, ALD presents a promising and efficient way of growing amorphous MoO_3 thin films. Still, mainly the *in-situ* growth and annealing behavior has been studied. [3] Therefore, we present a growth, structure and chemical analysis of as-deposited MoO_3 ALD thin films.

MoO_3 thin films were deposited on silicon with Beneq TFS-500 using $Mo(CO)_6$ and H_2O/O_3. The effect of precursor doses to the growth behavior and physical properties was studied immediately after the ALD with ellipsometry and later with XRR. Moreover, chemical and elemental analysis with ATR-FTIR and ToF-ERDA, respectively, were performed.

With ellipsometry, the ALD-window of the process was determined to be approximately in the range of 165-175 °C. Thus, deposition temperature of 170 °C was selected. The pulse time saturation of 55 °C heated $Mo(CO)_6$ was studied to take place around 2 s. The overlapping H_2O/O_3 pulsing time ratio in seconds was varied from 0/2-3/2. The O_3-only precursor yielded GPC of 0.65 Å/cycle and for the H_2O added pulses GPC was 0.75 Å/cycle. The ATR-FTIR spectra showed that unlike the other samples, the 2/2 mixture did not had an emphasized band at ~3650 cm^{-1} which is usually attributed to the presence of –OH groups.

The further studies suggest that prolonged storage of the samples in ambient conditions produced structurally differing surface layer on top of the original MoO_3 thin films. The XRR analysis showed a surface layer of 6 nm with a density of 2.8 g/cm^3 on average while the underneath MoO_3 layer showed density of 4.3 g/cm^3. Also, the refractive index value reduced on average from 2.03 to 1.90 between the fresh and aged samples. Moreover, the ToF-ERDA elemental depth profile results revealed that the C (2.5 at.%), H (14 at.%) and N (3.1 at.%) impurities are concentrated to the surface in the thin films. Still, the average O/Mo ratio was 3.1, being very close to stoichiometric.

Due to the presence of the parasitic surface layer, valid differences on the structural and elemental constitution of the different samples could not be identified. Therefore, this research concludes that the $Mo(CO)_6$ and H_2O/O_3 ALD thin films are not chemically stable in ambient conditions without further in-line-processing such as surface passivation.

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5:15pm **ALE+AF-MoA-16 Characterization of Al_2O_3 and HfO_2 Grown on Metal Surfaces with Thermal and Plasma Enhanced Atomic Layer Deposition**

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Atomic layer deposition (ALD) is potentially a very suitable deposition technology to grow ultra thin films with excellent thickness control, good conformity on high aspect ratio structures, and less defects. Al_2O_3 and HfO_2 are well-established high-k materials to replace SiO_2 in transistor and capacitor applications. To grow high quality ALD films with low leakage current, high breakdown electric field and dielectric constant, it is important to understand the impact of both plasma enhanced ALD (PEALD) with O_2-plasma and thermal ALD with H_2O on the interface between ALD film and substrate surface, and also the impact of the interface on the quality of ALD films.

We present the electrical and chemical characterizations of Al_2O_3 and HfO_2 films directly grown on Au, Ti and TiN surfaces. Metal Insulator Metal (MIM) capacitors with 10nm of Al_2O_3 or 10nm of HfO_2 as a dielectric layer were realized. Our results show that (1) the Al_2O_3 film grown by TMA metallic precursor and O_2-plasma has the highest breakdown electric field of 6.74 MV/cm, and the lowest leakage current of 8.6e-8 A/cm^2 at 2 MV/cm, which indicate that this 10nm of Al_2O_3 layer is high quality dielectric film with low pin-hole density and defects; (2) the HfO_2 film grown by TEMAH metallic precursor and H_2O has the lowest breakdown electric field of 3.95 MV/cm, and the highest leakage current of 7.6e-7 A/cm^2 at 2 MV/cm, which indicate that this 10nm of HfO_2 film has more pin-holes and defects; (3) the Al_2O_3 film grown by TMA and H_2O, and the HfO_2 film grown by TEMAH and O_2-plasma have the breakdown electric fields of 6.56 and 4.28 MV/cm, and the leakage currents of 2.40e-7 and 2.33e-7 A/cm^2 at 2 MV/cm, respectively; (4) both the Al_2O_3 and HfO_2 films grown by the PEALD with O_2-plasma show better qualities than that grown by the thermal ALD with H_2O; (5) the Al_2O_3 and HfO_2 with O_2-plasma processes do not show plasma-induced damage based on the tests of Van der Pauw (VdP) samples made from InGaAs-InAlAs layer structure with channels buried ~ 30 nm from the surface.

To further investigate, understand and optimize the ALD processes, Auger energy spectroscopy (AES) and high-resolution scanning Auger microscope (SAM) are used to analyze the chemical compositions and distributions in the interface between the ALD films (Al_2O_3 and HfO_2 grown with O_2-plasma and H_2O) and the metal surfaces (Au, Ti and TiN) without exposing the ALD films to air.

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