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

ALE-SuP-1 Mechanistic Thermal Desorption Studies of Thermal Dry Etching Reactions for Cobalt and Iron Thin Films, ***Mahsa Konh***, *A Teplyakov,* University of Delaware

Atomic layer etching of cobalt and iron has a number of important applications. The mechanisms of thermal dry etching of thin films of these metals were investigated using temperature programmed desorption (TPD) to understand surface chemistry involved in each reaction step. X-ray photoelectron spectroscopy (XPS) and microscopic investigations were used to characterize the surfaces obtained as a result of the etching process. Diketones, such as 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH) and 2,4-pentanedione (acacH), were tested as etchants. It was determined that in order for the volatile etching products to be formed, the films had to be oxidized or chlorinated, since clean surfaces resulted in decomposition of the diketonates. The oxidized surfaces were shown to evolve volatile transition metal-containing products at temperatures much higher compared to those on surfaces pre-exposed to Cl_2. However, the mechanism of the etching process appeared to be more complicated on chlorine-exposed surfaces. For example, a number of products of a general formula of $Co(hfac)_xCl_y$ were followed for hfacH reaction with cobalt films, and Co^{3+} was shown to participate in the process.

ALE-SuP-2 Mechanistic Study of the Thermal Atomic Layer Etch of Tungsten Metal Using O_2 and WCl_6, ***Suresh Kondati Natarajan***, *M Nolan,* Tyndall National Institute, Ireland*; P Theofanis, C Mokhtarzadeh, S Clendenning,* Intel Corp.

In semiconductor devices, the low electrical resistivity of tungsten coupled with its high resistance to electromigration have driven its use in contacts between transistor source/drains and higher layer interconnects. However, due to the diminishing dimensions of such devices, the need for precision controlled monolayer etch processes have become a necessity so as to enable current and future device architectures. Accordingly, Atomic Layer Etch (ALE) functions as a complementary process technique to well-established Atomic Layer Deposition (ALD) methodologies, such that sequential self-limiting etch processes can be targeted with the desired monolayer control for ultra-thin film material removal. Recently, thermal ALE processes for W have been reported by Parsons and co-workers[1,2] in which the W is first oxidized by a pulse of O_2 or O_3 gas and then the oxidized material is subsequently removed via gas phase pulses of WF_6 or WCl_6.

Herein, we present a first principles based computational analysis of this thermal ALE process for W metal using an oxidation step followed by introduction of WCl_6 as a co-reactant. We have investigated oxidants for the first pulse in the ALE sequence including O_2, N_2O and H_2O_2. It is shown that bulk oxidation of W is not spontaneous, but coverage of the W surface is dependent and subject to thermodynamic barriers of approximately 2 eV. The energetics associated with the removal of possible volatile etch species in the second ALE step such as $WOCl_4$ and WO_2Cl_2 will be presented. Additionally, the use of Cl_2 gas as an alternative to WCl_6 in the second ALE step has also been explored. A full reaction mechanism for these thermal atomic layer etch processes will be discussed.

1. Xie, W., Lemaire, P. C., Parsons, G. N. Thermally Driven Self-Limiting Atomic Layer Etching of Metallic Tungsten Using WF_6 and O_2. ACS Appl. Mater. & Interfaces, 2018, 10, 9147–9154.

2. Xie, W., Lemaire, P., Parsons, G.N. Self-Limiting Thermal Atomic Layer Etching of Tungsten Metal Using O_2 Oxidation and WCl_6 or WF_6: Role of Halogen Species in Temperature Dependence of ALE Reaction Rate. AVS ALE Workshop, 2018, Incheon, South Korea.

ALE-SuP-3 Using Etching of the Atomic Layer to Remove Damaged Layers Obtained by Plasma-Chemical Etching with Subsequent Growth of GaAs Quantum Dots by the Method of Droplet Epitaxy, ***Victor Klimin***, *A Rezvan, O Ageev,* Southern Federal University, Russia

The task of controlled synthesis of semiconductor self-organizing nanostructures - quantum dots, filamentous nanocrystals, metallic nanodroplets - is extremely important, first of all, to create effective sources of single and entangled photons - the basis of quantum cryptography systems, as well as functional elements based on filamentary nanocrystals, single quantum dots and / or their complexes with a given topology, on the basis of which cellular automata, memory elements, integrated photonics and functional blocks quantum computing systems [1-3].

At the same time, drip epitaxy, based on separate deposition of components of groups III and V, allows not only to significantly expand the range of structures formed (quantum dots, rings, disks and complex, hybrid structures based on them), but also to realize independent control of the density and size of quantum dots, as well as to use for their creation virtually any A3B5 system, which is inaccessible to techniques based on the Stranski – Krastanov mechanism.

The use of structured GaAs and Si substrates and the features of droplet epitaxy techniques will effectively localize epitaxial growth at given points on the surface, thereby ensuring precise positioning and control of the parameters of synthesized nanostructures — metal nanoscale droplets (catalytic centers) and quantum dots based on them (in the case of GaAs).

The structuring of the substrates was carried out by a combination of methods of focused ion beams and plasma-chemical etching. However, after obtaining substrates with nanoscale relief, a broken layer was formed on the surface in the depressions caused by plasma and penetration of Ga ions after exposure to focused beams. To remove damaged layers, the best method is layer-by-layer etching of the GaAs surface [4].

To determine the penetration depth of gallium ions, a simulation was carried out and it was revealed that after treatment in chlorine plasma, 12 atomic disturbed layers remain, which were later removed using the atomic layer etching method. When using the “soft” etching mode, the angle of inclination of the nanoscale structures changed and the growth of quantum dots did not occur.

At the end of the experimental studies, samples were obtained with nanoscale surface profiling, a combination of methods of focused ion beams, plasma chemical etching, atomic layer etching, in which GsAs quantum dots were obtained by dropping epitaxy.

This work was carried out as part of a study conducted in the framework of the projects of the Russian Science Foundation No. 15-19-10006.

ALE-SuP-4 Atomic Layer Etching of Silicon Using a Conventional ICP Etch Chamber for Failure Analysis Applications, ***John Mudrick***, *R Shul, K Greth, R Goeke, D Adams,* Sandia National Laboratories

Silicon removal with true atomic fidelity has been shown to require fine control of reactant species concentrations, ion energies, and chamber conditioning. Such fine control of these process parameters is not straightforward to achieve, nor to verify, on legacy process equipment. This work highlights progress toward achieving atomic layer etching (ALE) of silicon wafers and packaged die in standard Cl_2/Ar plasma chemistry for failure analysis applications. Wafer-scale etch experiments show an etch rate decrease to below 1 nm/cycle with decreasing substrate temperature and Cl_2 surface modification step time, however the etch rate increases with the number of etch cycles due to insufficient control over Cl_2 reactant supply; this is especially problematic for silicon removal depths above a few hundred nm, required for failure analysis application. We will use time-resolved optical emission spectroscopy to demonstrate best-case reactant control in this system and suggest methods for achieving ALE-like etching. Furthermore, we observe that the D.C. voltage bias generated during the surface modification and sputter steps is significantly above target values during the first few seconds after plasma ignition for both steps. We have developed multi-step ignition schemes for both stages to ensure smooth transitions where the voltage bias remains very near zero during the Cl_2 plasma generation step and below the sputter threshold of the modified surface layer(s) during the sputter desorption step. For packaged die processing, we show that silicon removal is strongly dependent on both the carrier substrate type as well as die mounting scheme. Using the best developed method, we will present cross-section microscope images showing back-side handle silicon removal to within a few hundred nanometers of the still-functional active device area.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.This paper describes objective technical results and analysis. Any subjective views or opinions that might beexpressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

ALE-SuP-5 Study of the Chemical Fabrication Process of NSOM Probes and the Modification of its Surface for Sensing Applications*, **Muhammad Nazmul Hussain**, J Woehl,* University of Wisconsin-Milwaukee

Near-field scanning optical microscopy (NSOM) provides us with eyes for the nanoworld by combining the potentials of scanning probe technology with the power of optical microscopy. To acquire optical images beyond the diffraction limit, NSOM probes require a sub-wavelength optical aperture with wide cone angle of the probe for efficiently channeling the illumination light to the tip apex. Between the two NSOM aperture probe fabrication methods, chemical etching creates tips with wider cone angles of the probe. To determine the mechanism of probe formation and optimize the cone angle with the chemical etching method, different etching times were studied. Additionally, the NSOM probe surface was modified with different fluorescent compounds for high-resolution, fluorescence-based chemical sensing applications.

ALE-SuP-6 A Mechanistic Study of the HF Pulse in the Thermal Atomic Layer Etch of HfO_2 and ZrO_2*, **Rita Mullins**, S Kondati Natarajan, M Nolan,* Tyndall National Institute, Ireland

Thermal atomic layer etching (ALE) of HfO_2 and ZrO_2 uses sequential and self-limiting fluorination reactions using HF as the reactant. This modern approach for ALE is the reverse of atomic layer deposition (ALD) and leads to isotropic etching that removes the modified layer. Each cycle of thermal ALE consists of two precursor pulses. In the first pulse the precursor reacts with the surface atoms of the substrate material and forms a stable and non-volatile layer, this surface modification is self-limiting in nature. We present a first principles study of the hydrogen fluoride pulse in the first step in thermal atomic layer etch of monoclinic hafnium dioxide and zirconium dioxide using density functional theory (DFT) calculations. HF molecules adsorb on the surfaces of these metal oxides by forming hydrogen bonds and may remain intact or dissociate to form, Hf-F and O-H for hafnium dioxide and Zr-F and O-H for zirconium dioxide. The adsorption of one HF molecule at the bare surface of both metal oxides results in dissociative adsorption at all binding sites. The adsorbed H atom can migrate to other O sites on the bare surface depending on energetic barriers. For multiple HF adsorption at coverages ranging from 1/16 to 1 monolayer we find mixed molecular and dissociative adsorption of HF molecules at the bare surfaces. The energetic barriers involved for the formation of H_2O from the HF pulse are estimated using the CI-NEB method.

ALE-SuP-7 Atomic Precision Processing of Aluminum Mirrors for Enhanced Ultra-violet Optical Properties*, **Scott Walton**, A Kozen,* U.S. Naval Research Laboratory*; J del Hoyo, M Quijada,* NASA Goddard Space Flight Center*; D Boris,* U.S. Naval Research Laboratory

Astronomical measurements in the Far Ultra-violet (FUV, 90-200 nm) require the use of aluminum thin films due to aluminum's high reflectivity over this wavelength range. Unfortunately, the native aluminum oxide layer formed in atmosphere is strongly absorbing in this wavelength range, requiring that the aluminum films be passivated with a dielectric that inhibits oxidation. Due to the fast oxidation of aluminum, a simultaneous etch and deposition process is desirable to both eliminate the native aluminum oxide after growth and replace it with a different passivation coating layer. Optical measurements in the FUV range are some of the most challenging due to limited selection of low reflectivity coatings available for use on aluminum thin films. Typically magnesium fluoride (MgF_2) or lithium fluoride (LiF) coatings are used for these passivation purposes but each has its problems. MgF_2 has an absorption cutoff at 115 nm occluding a critical part of the FUV spectrum. LiF has a lower absorption cutoff at 102.5 nm, but is hygroscopic and thus susceptible to degradation in ambient conditions. A promising alternative to these coating materials is AlF_3, which theoretically can provide reflectivity greater than 50% down to 100 nm if the coating is sufficiently thin. In this work, we explore the use of electron beam generated plasmas to simultaneously etch the native oxide layer from aluminum thin films while depositing an AlF_3 capping layer to passivate the aluminum reflector. XPS measurements indicate that this approach is cable of producing very thin (<5 nm) AlF_3 films with some mild oxygen contamination. We will discuss the impact of plasma power, chemistry, and time on the composition and structure of the passivating layer and its subsequent optical properties. This work is supported by the Naval Research Laboratory base program and NASA Strategic Astrophysics Technology (SAT) grant No. NNH177ZDA001N.

ALE-SuP-8 Surface Reaction Analysis for Atomic-Layer Etching and Deposition by Means of Beam Experiments*, **Kazuhiro Karahashi**, T Ito, S Hamaguchi,* Osaka University, Japan

As the sizes of semiconductor devices continue to diminish, atomically controlled damage-less selective etching processes are absolutely crucial for the fabrication of such devices. Ligand-exchange processes of organic compounds deposited on metal surfaces, and low-energy ion or cluster beam processes are candidates for such highly selective precise etching processes. For the control of these processes, it is important to understand and control surface reactions of organic compounds and low-energy ions/clusters. Molecular beam experiments provide an understanding of the dynamics and kinetics of chemical interactions of gas molecules with solid surfaces. In this study, a new surface-reaction analysis system with molecular beams has been developed for the analyses of etching reactions. The system has differentially-pumped beam sources for low-energy ions, thermal-molecular and metastable radicals/clusters that independently irradiate the sample surface set in an ultra-high-vacuum (UHV) chamber. To study surface reactions, we detected the scattered species and desorbed products with a differentially pumped quadrupole mass spectrometer (QMS) and measured adsorbed chemical states on the surface during various beam irradiation by X-ray photoelectron spectroscopy (XPS). The QMS provided time-resolved measurements and could be synchronized with an ion or molecular beam. The system can experimentally simulate an atomically controlled process such as atomic layer etching (ALE) or atomic layer deposition (ALD). Also presented as sample experimental data obtained in this system are desorbed species, and surface chemical states during beam irradiation of transition metal (Ni, Cu etc.) surfaces with halogen and organic molecules (such as diketone).

ALE-SuP-9 Atomic Layer Etching of SiO_2 and Si_3N_4 with Fluorocarbon, Hydrofluorocarbon and Fluoroether Compounds*, H Chae, **Yongjae Kim**, T Cha, Y Cho,* Sungkyunkwan University (SKKU), Republic of Korea

Nanometer and angstrom scale etching is getting more critical as the critical dimension of semiconductor devices shrinks down to 10nm. Atomic layer etching (ALE) processes are being developed and studied to control etch depth in nanoscale and atomic scale by limiting the amounts of chemical reactants available on the surface with self-limited reactions. [1] With cyclic ALE processes, low surface roughness, high uniformity and high selectivity can be achieved with low damage to devices. [2-3]

In this work, cyclic plasma etching for SiO_2 and Si_3N_4 was developed and characterized with surface modification in an inductively coupled plasma (ICP) reactor with fluorocarbon, hydrofluorocarbon, and fluoro-ether plasmas. The process consists of two steps of surface modification and removal step. In the first step, thin fluoro- or hydrofluro-carbon layers are deposited on SiO_2 and Si_3N_4 surface with fluorocarbon, hydrofluorocarbon, and fluoroether plasmas. In the second step, the modified layers are removed with ions or radicals generated from Ar or O_2 plasmas. At the bias voltage increased, the incomplete etched region, the self-limiting etched region, and the sputtering region appeared, and lower etching rate was obtained using O_2 plasma than Ar plasma. Etching rate were compared at various conditions of reaction gases and plasma power and the rate could be controlled under 10 Å/cycle. Etching rate dependences are investigated on ion energy, etching time, FC film deposition, and precursor selection. Self-limited etching rate was obtained and higher selectivities of SiO_2/Si and Si_3N_4/Si etch rate were obtained with fluoroether.

References

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[3] K. Koh, Y. Kim, C.Kim, and H. Chae, J. Vac. Sci. Technol. A, 36, 01B106 (2018)

ALE-SuP-10 Cyclic Etching of Copper Thin Films using Two Sequential Steps*, **Eun Tack Lim**, J Choi, J Ryu, M Cha, C Chung,* Inha University, Republic of Korea

Copper has been used as the interconnects in the semiconductor memory devices because it has many advantages such as low resistance and low diffusivity. In addition, the electromigration phenomenon which causes wire deformation and breakage occurs less on copper [1]. Currently, copper has been etched through a damascene process because direct dry etching process has not been developed. However, the damascene process reveals some limitations in achieving fine patterns of several nanometers [2]. To solve this issue regarding the damascene process, the intense studies on

copper patterning are being performed using conventional dry etching.Cyclic etching, as another approach to etch the copper films, can be a prospective etching technique. Cyclic etching including surface modification and its removal can provide the good etching performance of copper films by effectively inducing surface reaction and precisely controlling the etch depth. These results are attributed to the nature of self-limiting process and the removal of the film by layer-by-layer. There are possible various gas combinations in cyclic etching of copper films. In this study, cyclic etching with two sequential steps of surface modification and ion bombardment was performed. The surface modification and etch depth (etch rate) of copper film were confirmed using surface profilometer, scanning probe microscopy, and field emission scanning electron microscopy (FESEM) as a function of various parameters such as the time of surface modification (plasma exposure) and the bombardment energy of ions. Besides, the resultant etch profile and etch mechanism of copper film in the cyclic etching have been investigated by FESEM, X-ray photoelectron spectroscopy, and Raman spectroscopy.

Acknowledgments This research was supported by the MOTIE(Ministry of Trade, Industry & Energy (10080450) and KSRC(Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

References[1] A. Strandjord, S. Popelar, C. Jauernig, Microelectron. Reliab. **42,** 265–283(2002) [2] H. Helneder, H. Ko¨rner, A. Mitchell, M. Schwerd, U. Seidel, Microelectron. Eng. **55**, 257–268 (2001)

ALE-SuP-11 Analysis of Mechanisms Involved in Cryogenic ALE*, **Thomas Tillocher**, G Antoun, P Lefaucheux, R Dussart,* GREMI Université d'Orléans/CNRS, France*; K Yamazaki, K Yatsuda,* Tokyo Electron Limited, Japan*; J Faguet, K Maekawa,* TEL Technology Center, America, LLC

Atomic Layer Etching (ALE) has been developed almost 40 years ago, but has gained interest these last years for micro and nanoelectronic processes where high precision patterning is required. ALE consists in a sequential process relying on the self-limited adsorption of precursor radicals on the first monolayer(s) of material to be etched. Then, under a low energy ion bombardment, the etch products form and desorb until the adsorbed layer is depleted. This self-limited reaction removes a few monolayers. By repeating the cycle, the material is etched a few monolayers by a few monolayers.

ALE of SiO_2 has been achieved with a 3-step process and reported in the literature [1]. The first step is an Ar/C_4F_8 plasma without any ion bombardment. The oxide surface is then coated with a very thin fluorocarbon layer. The second step is a pure Ar plasma still with no RF self-bias voltage where C_4F_8 is pumped 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 etch step can be self-limited.

Although quasi-ALE of SiO_2 has been demonstrated with this process, fluorocarbon contamination of chamber walls is an issue. This affects the reproducibility of ALE processes and hence chamber cleaning is required. Cryogenic Atomic Layer Etching (Cryo-ALE) is proposed as a potential solution. In this new process, the substrate is cooled to very low temperature by liquid nitrogen. The plasma phase deposition step is replaced by a physisorption step consisting in exposing the cooled substrate to a fluorocarbon gas flow. Under such conditions, species are adsorbed only at the cooled surface and hence wall pollution is mainly suppressed. Cryo-ALE of SiO_2 has been shown to be effective at -120°C. The details regarding the overall process are presented in G. Antoun's abstract.

If the temperatures is raised of a few degrees (for instance to -110°C), no etching is observed since C_4F_8 does not significantly physisorb at such temperature. Therefore, understanding physisorption conditions as well as activation of etching using a physisorbed layer is relevant for a better control of the process. Desorption mass spectrometry experiments will be fully presented and discussed in this paper.

[1] Metzler et al., J. Vac. Sci. Technol. A 32(2), 020603-1 2014

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ALE-SuP-12 Study on Dry Etching Characteristics of Germanium Oxide by Atomic Layer Deposition*, **Donghyuk Shin**, J Jeong, H Song, H Park, D Ko,* Yonsei University, Republic of Korea

While the Si-based electronics whose basis materials consisting of silicon substrate and silicon dioxide, have played a leading role in the semiconductor industry, germanium has also been receiving steady attention as a new channel material for its high carrier mobility. In particular, the studies on germanium oxide films of which the most are discussing mainly the Ge oxidation process on Ge substrates, have been conducted for several decades. However, the formation of GeO_2 film through the oxidation process restricts its own potential for utilization because it is only applicable on Ge substrates. Oxidation process conducted on the SiGe layer causes Ge condensation at its interface where Ge atoms remain nonbonded to oxygen due to the less negative Gibbs free energy to form the GeO_2 compared to SiO_2. In this context, the growth of GeO_2 film by the atomic layer deposition (ALD) enables its utilization to be enlarged even for use on Si substrate. For example, a literature examined the applicability of ALD GeO_2 film on Si substrate as a secure memory device employing its unusual film property of dissolving in water. However, the GeO_2 film inevitably exhibits unstable nature under the wet etching process, which means that the fundamental study on the GeO_2 film needs further explorations including dry etch characteristics.

In this talk, we discuss the growth and characterizations of GeO_2 film by ALD process. Film properties of ALD GeO_2 were evaluated using High-resolution X-ray photoelectron spectroscopy and Auger electron spectroscopy. We demonstrate the dry etch characteristics of ALD GeO_2 films. Dry etch test was performed in the reactive ion etching chamber equipped with a direct capacitive-coupled plasma, using C/F based dry etch chemistry. In addition, the dry etch mechanism of the ALD GeO_2 film was investigated in comparison with thermal oxide and silicon nitride. Basic dry etching selectivity mechanism between SiO_2 and Si_3N_4 lies on the different ability of each film to self-consume the polymer barrier layer which is formed during dry etching process using C/F based plasma. Our dry etch test results showing a faster dry etch rate for Si_3N_4 film against SiO_2 film during the reactive ion etching, are in good agreement with the exper imental results reported in literatures, while the ALD GeO_2 film reveals its dry etch characteristics which encompass the competing reaction between etching and polymerization.

ALE-SuP-13 Laser Isotropic Atomistic Removal of Germanium*, D Paeng, **He Zhang**, Y Kim,* Lam Research Corp.

Pico second (ps) pulsed laser has been used to achieve isotropic atomistic removal of germanium (Ge). After hydrogen (H_2) plasma pre-treatment at room temperature, adsorption of O_2 or Cl_2 gas on the clean Ge surface is used to form germanium monoxide (GeO) or germanium chloride ($GeCl_x$) layer. Under laser irradiation, modified layer will heat up rapidly depending on the laser fluence. This surface oxide or halide desorbs thermally, and the short pulse of the ps laser suppresses heat diffusion into the material enabling surface-confined photo-thermal reactions on an ultrafast time scale without thermal budget issue. Etch rates (ER) of sub-nanometers per cycle have been achieved. We report on parametric studies showing how the laser parameters and process conditions affect the ER and the surface roughness after etching.

ALE-SuP-14 Anisotropic Atomic Layer Etching of Tungsten using Reactive Ion Beam*, **Doo San Kim**, J Kim, W Lee, Y Gill, B Jeong, G Yeom,* Sungkyunkwan University, Republic of Korea

Atomic layer etching (ALE) is a next generation etching technique consisting of cyclic removal of a monolayer per cycle by repeating adsorption and desorption steps. ALE has advantages such as precise thickness control, high etch selectivity, surface smoothing effect, and minimization of the surface damage during the etching. For the fabrication of next generation nanoscale devices, both isotropic and anisotropic ALE techniques are required. In this study, anisotropic ALE of tungsten (W), which is used as an interconnect layer and the gate material of semiconductor devices, was investigated by sequentially exposing to F radicals by NF_3 plasma to form a tungsten fluoride layer followed by the exposure to an oxygen ion beam to remove the tungsten fluoride layer by forming volatile tungsten oxyfluoride (WO_xF_y) compound at room temperature. The result showed that, at optimized ALE conditions, a precise etch rate of ~ 2.6 Å/cycle was obtained while increasing the W etch depth linearly with increasing the number of etch cycles. And, the W ALE mechanism was investigated by analyzing the surface roughness and surface composition of W during the adsorption step and desorption step.

Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE1-MoA
Energy-enhanced ALE

Moderators: Keren J. Kanarik, Lam Research Corp., Harm Knoops, Eindhoven University of Technology

1:30pm **ALE1-MoA-1 Atomic Layer Etching – Advancing Its Application with a New Regime*, Samantha Tan**, W Yang, K Kanarik, Y Pan, R Gottscho,* Lam Research Corp. **INVITED**

Continued shrinking of device dimensions has placed extreme requirements on plasma etching technology, making it increasingly challenging to faithfully transfer patterns with nanometer-sized features. To address this nanoscopic challenge, atomic layer etching (ALE) has been successfully used to extend conventional etch technology and some critical processes have been implemented in high-volume manufacturing (HVM) [1]. To be adopted for more applications, ALE must further overcome both productivity and technical limitations. Directional ALE typically operates in a low energy (< 100 eV) regime which results in relatively low etch rates (~5 Å /cycle). Productivity can be improved by engineering hardware to increase switching speed – but there is room for improvement. In addition, ALE faces technical limitations in applications where synergy is < 100 % which can result in sidewall etching. This is particularly problematic for maintaining a directional etch profile in high aspect ratio features. In this talk, we will present results obtained using a new operating regime that has the potential to meet the productivity and technical challenges for ALE while retaining its inherent benefits: low damage, smoothing, aspect ratio independence, and selectivity [2, 3].

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[2] K. Kanarik, S. Tan, and R. A. Gottscho, J. Phys. Chem. Lett. 2018, 9, pp. 4814–4821>

[3] Michael Koltonski, Wenbing Yang, Craig Huffman, Mohand Brouri and Samantha Tan, "Opportunities and Challenges Utilizing Atomic Layer Etch for Lead Edge Technology Metal Line Widths", SPIE Advanced Lithography Conference, San Jose, CA, Feb 24-28, 2019>

2:00pm **ALE1-MoA-3 Control of the Interface Layer in ALE Process by Alternating O_2 Plasma with Fluorocarbon Deposition for High Selectivity Etching*, Takayoshi Tsutsumi**, A Kobayashi,* Nagoya University, Japan*; N Kobayashi,* ASM Japan K.K., Japan*; M Hori,* Nagoya University, Japan

Our research group developed a process for atomic layer etching of an SiO_2 film using alternating nanometer-thick fluorocarbon film deposition and O_2 plasma irradiation [1]. This process allows the atomic scale etching of SiO_{-2} with high reproducibility because of removing extra carbon on surface and cleaning chamber walls by O_2 plasma. The ALE process could have benefits for etching SiO_2 selective to Si_3N_4 if we actively control the chemistry in the mixture region between Si-compounds and fluorocarbon, and suppress the oxidation of Si_3N_4 by O_2 plasma.

In this time, the ALE process was performed to a SiO_2 and Si_3N_4 deposited by ALD process in a capacitively coupled plasma (CCP) reactor. A 100-MHz electrical power of 100 W was applied to the upper electrode at a pressures of 2.0 Pa. The wafer temperature was set at 20°C. For the deposition process, C_4F_8/Ar plasma was used to form a fluorocarbon film. Figure 1 shows the C 1s spectra of a SiO_2 and Si_3N_4 after the deposition processes. The C 1s spectrum of SiO_{-2} after the deposition process exhibits C-C, C-CF_x, CF, CF_2, and CF_3 peaks. On the other hands, the spectrum of Si_3N_4 shows an increased in the fraction of the C-C bond and exhibits the Si-C bond. Higher fraction of the C-C and forming Si-C and C-N bonds in the mixture regions lead to etching SiO_{-2} selective to $Si_{-3}N_4$. Higher F/C ratio in fluorocarbon film is required for etching SiC compared to SiO_2 and Si_3N_4 because of etching products of SiF_4 with very little SiF and SiF_2[2]. Moreover, higher bond energies of CN, which are C-N of 305 kJ/mol, C=N of 615 kJ/mol and C≡N of 887 kJ/mol, could suppress oxidation of SiN by control of ion energy and wafer temperature. If the oxidation by O_2 plasma is suppressed, our ALE by alternating fluorocarbon deposition and O_2 plasma could apply to industry process for next-generation devices due to high controllability and reproducibility. We analyze the depth profiles of atomic concentrations in the mixture regions for a SiO_2 and Si_3N_4 by angle resolved X-ray photoelectron spectroscopy (XPS) to control chemistry of the mixture regions by some knobs such as ion energy and surface temperature.

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2:15pm **ALE1-MoA-4 Self-limiting Atomic Layer Etching of SiO_2 using Low Temperature Cyclic Ar/CHF_3 Plasma*, Stefano Dallorto*,** Lawrence Berkeley National Laboratory*; A Goodyear, M Cooke,* Oxford Instruments Plasma Technology, UK*; S Dhuey,* Lawrence Berkeley National Laboratory*; J Szornel,* Lawrence Livermore National Laboratory*; I Rangelow,* Ilmenau University of Technology, Germany*; S Cabrini,* Lawrence Berkeley National Laboratory

Single digit nanometer semiconductor manufacturing is increasingly demanding atomic scale process controllability to further decrease critical dimensions and pitches. High etching precision and material selectivity become essential in the atomic scale era. Plasma based atomic layer etching (ALE) shows promise to attain atomic etch precision, enhancing energy control and reaction chemistry control.

Here we study a Fluorocarbon(FC)-based ALE process for controlling the etching of silicon dioxide at the atomic level. Figure 1 shows the schematic of atomic layer etching process using Ar plasma and CHF_3 gas. In this technique, an Ar plasma is maintained continuously through the process, below the energy threshold for SiO_2 sputtering. A fluorocarbon chemistry is then introduced via CHF_3 pulsing to provide the reactant absorption. Subsequently, once the gas pulse has concluded, bias power is introduced to the Ar plasma, to provide enough energy to initiate reaction of the FC with the SiO_2. In ideal ALE, each of the steps is fully self-limiting for over exposure to increase uniformity on the microscale (wafer) and atomic scale.

With the goal of achieving self-limiting FC-based ALE, we investigated the etch step using low energy Ar ion bombardment. By carefully tailoring the energy of ion bombardment, it is possible to control the etching depth to approach a self-limiting behavior. The impact of various process parameters on the etch performance is established. We demonstrated that the SiO_2 amount etched per cycle (EPC) is strongly affected by the forward bias plasma power, as well as the substrate temperature (Figure 1(a)). The substrate temperature has been shown to play an especially significant role, at -10 °C the contributions to chemical etching coming from fluorine and fluorocarbon compounds from chamber walls are minimized and a quasi-self-limiting behavior ALE is observed.

Figure 1(b)-(f) showed the Cr features after being etched for 60 ALE cycles with the optimal ALE self-limiting conditions. Feature trenches vary from 20-200 nm and were defined using metal lift-off. Overall, using the cyclic CHF_3/Ar ALE at -10 °C, we reduced geometric loading effects during etching and reached aspect ratio independent etching, with great potential for significant improvement in future etching performances.

2:30pm **ALE1-MoA-5 Evolution of Photoresist Layer Structure and Surface Morphology in a Fluorocarbon-Plasma-Based Atomic Layer Etching Process*, Adam Pranda**, K Lin, S Gutierrez Razo, J Fourkas, G Oehrlein,* University of Maryland

The impact of continuous-wave plasmas in realizing a pattern transfer process with a Ar/fluorocarbon composition on photoresist etching behavior and surface roughness development has been extensively studied.[1] However, the characteristics of photoresists under atomic layer etching (ALE) processes have not been well established. Specifically, the structure and morphology of the photoresist layer is dependent on the interplay between energetic ion bombardment and the diffusion of reactive species at the surface. For evaluating these photoresist properties, we used an ALE process with an Ar carrier gas and a fluorocarbon (FC) precursor gas, for example C_4F_8.[2]

For sample characterization, we utilized a combination of real-time, *in situ* ellipsometry and post-process surface roughness and surface chemistry analysis using atomic force microscopy (AFM) and x-ray photoelectron spectroscopy, respectively. The AFM characterization provided information on both the surface roughness magnitude as well as the distribution via a power spectral density analysis. Both an industry-standard 193 nm photoresist and an extreme ultraviolet (EUV) photoresist were evaluated.

Based on the ellipsometric characterization, we find that the 193 nm photoresist initially develops a surface dense amorphous carbon (DAC) layer from Ar ion bombardment of both the native photoresist and deposited FC, which contributes additional carbon to the DAC layer, increasing its thickness. Upon the FC deposition step in the ALE process, the refractive index of the DAC layer decreases due to fluorine diffusing into the layer structure. Corresponding AFM analysis shows a reduction in

the surface roughness. Once the DAC layer becomes saturated with fluorine, a discrete FC layer forms on the surface. Subsequently, in the etching step, the discrete FC layer is removed, the DAC layer recovers its thickness, and the cycle repeats.

The authors gratefully acknowledge Eike Beyer for assistance with the experimental setup, R. L. Bruce, S. Engelmann, and E. A. Joseph for supplying the EUV materials, and financial support of this work by the National Science Foundation (NSF CMMI-1449309) and Semiconductor Research Corporation (2017-NM-2726).

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2:45pm **ALE1-MoA-6 Optimized Radical Composition of C4F8/Ar Plasma to Improve Atomic Layer Etching of SiO_2**, ***Young-Seok Lee**, J Lee, S Yoo, S Lee, I Seong, C Cho, S Kim, J Son, S You,* Chungnam National University, Korea

For the last decade, there was a big step in atomic layer etching (ALE) of SiO_2 with fluorocarbon plasma. After a computer simulation suggested a surface modification method via fluorocarbon film deposition on SiO_2 and its atomically thin removal, ALE of SiO_2 was demonstrated experimentally using an inductively coupled fluorocarbon plasma. Ever since, there have been a lot of research trying to improve the ALE of SiO_2. Meanwhile, it was also found that a fluorocarbon film deposited during deposition-based SiO_2 ALE is formed from fluorocarbon neutral radicals as well as low-energy ions. Their compositions therefore are expected to play a significant role to determine characteristics of the deposited fluorocarbon film and, in the end, the result of ALE of SiO_2. For an investigation into an optimized composition of the fluorocarbon plasma components, we measured neutral radical densities under various conditions using a quadrupole mass spectrometer and monitored SiO_2 thickness changes during ALE in real time with in situ multi-wavelength ellipsometer. An improved SiO_2 ALE process and possible improvement mechanisms will be presented.

3:00pm **ALE1-MoA-7 Atomic Layer Etching of Silicon Nitride with Ultrahigh Etching Selectivity over Silicon and Oxide Materials by Utilizing Novel Etch Gas Molecule**, ***Xiangyu Guo,*** American Air Liquide*; N Stafford,* Air Liquide*; V Pallem,* American Air Liquide

Silicon nitride etching with high selectivity over silicon and silicon oxide material, without or with minimal damage to the exposed surfaces, is one of the most critical processes in the fabrication of complementary metal-oxide-semiconductor (CMOS) devices. In this work, the authors propose a novel hydrofluorocarbon etch gas molecule for Si3N4 etching with ultrahigh etching selectivity over Si materials (p-Si, SiO2, SiON, SiCN, etc) based on atomic layer etching (ALE) cyclic process. Each cycle of the ALE process consists two independent unit process reactions: step A - polymer deposition and step B - removal step. The process was conducted in a home-built capacitively coupled plasma (CCP) chamber and was optimized on planar thin films first. CH3F was used as the process baseline. The authors show that novel gas molecule demonstrates significant improved performance in several aspects comparing to CH3F - ultrahigh selectivity, minimal damage, smoother surface after etching, higher ALE synergy, etc. The new molecule was also evaluated on patterned structure - Si3N4 gate spacer. The authors demonstrate the ALE process utilizing proposed novel hydrofluorocarbon molecule outperforms typical spacer process, in particular, with better etch profile control - the spacer footing can be reduced more than 70%, and with minimal nitride sidewall thinning. The authors also show that due to the ultrahigh etch selectivity, damages to Si substrate was minimized, as evidenced by further surface elements characterization - no formation of Si-C/SiO. Surface smoothing effect was also observed after the etch process with the novel gas molecule. Because of these advantages, the proposed novel hydrofluorocarbon etch gas is a very promising candidate for spacer patterning, to enable further CD and pitch downscaling of the CMOS device.

3:15pm **ALE1-MoA-8 Atomic Layer Etching at Low Substrate Temperature**, ***Gaëlle Antoun,** T Tillocher, P Lefaucheux, R Dussart,* GREMI Université d'Orléans/CNRS, France*; K Yamazaki, K Yatsuda,* Tokyo Electron Limited, Japan*; J Faguet, K Maekawa,* TEL Technology Center, America, LLC

Semiconductor industry has followed Moore's law through years. Nowadays, industry and researchers are trying to reach nanoscale dimensions to continue the trend "beyond Moore's Law".

In this framework appeared atomic layer etching (ALE) where self-limited etching is performed, for instance, on SiO_2, using C_4F_8/Ar plasma [1]. In this process, CF_x monolayers are deposited on the surface before etching.

In order to perform ALE cycles without reactor wall contamination by CF_x species, ALE process is proposed at low substrate temperature. In our experimental protocol, fluorocarbon gas such as C_4F_8, is physisorbed at the sample surface in a first step. Then, in a second step, etching is performed by Ar plasma.

The experiments were carried out in an inductively coupled plasma reactor. Tests were performed on three different samples (SiO_2, Si_3N_4, and a-Si) that were glued on a carrier wafer. Then, they were cooled down to very low temperature by liquid nitrogen. In-situ spectroscopic ellipsometry was used to follow the layer thickness evolution of the central sample. The other samples were characterized ex-situ after the experiment. Surface roughness evolution before and after etching was checked by performing atomic force microscopy (AFM).

Finally, Langmuir probe and Quadrupole Mass Spectrometry (QMS) were used to better understand the involved mechanisms.

The aim of the first tests was to prove that etching occurs only at low temperature when using fluorocarbon gas flow. For that, the same etching test was performed at -120°C and few degrees above. At -110°C, etching is very limited, which shows that physisorption is not as significant as at -120°C. However, at –120°C, a few monolayers of C_4F_8 can be physisorbed and etching with Ar plasma has been observed thereafter.

Then, the main goals of this research was to reach self-limited etching regime and get an identical etching rate through cycles. To this end, the influence of various parameters of the process were examined. Different step times and pressures were studied to understand physisorption mechanisms. Temperature effect on species residence time was also evaluated using in-situ ellipsometry and QMS. In order to limit physical sputtering by ion bombardment and reach self-limited etching, different plasma parameters , such as self-bias, ICP power and step time, were studied. The etch per cycle is typically between 0.2 and 0.5 nm depending on the process parameters. The different steps of deposition, purge and etching can be clearly identified by ellipsometry.

Acknowledgments

The authors gratefully thank S.Tahara for his helpful discussions.

1. Metzler et al., J. Vac. Sci. Technol. A 32(2), 020603-1 2014

Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE2-MoA
ALE of Compound Semiconductors

Moderators: David Boris, U.S. Naval Research Laboratory, Ishii Yohei, Hitachi High Technologies

4:00pm **ALE2-MoA-11 Developments of Atomic Layer Etch Processes and their Applications in Fabricating III-V Compound Semiconductor Devices**, ***Xu Li,** Y Fu, S Cho, D Hemakumara, K Floros, D Moran, I Thayne,* University of Glasgow, UK **INVITED**

In recent years, atomic layer etch (ALE) to precisely remove very thin layers of materials using sequential self-limiting reactions has attracted extensive attention in semiconductor processing. Our work has indicated that ALE processes have versatile potential in the fabrication of III-V compound semiconductor devices, a number of which will be discussed in this presentation. One example is the use of an ALE process for precise control of the threshold voltage of GaN-based power transistors. This enables both normally off and normally on devices to be realised on the same wafer, which a vital for the realisation of an integrated cascode transistor (Fig 2). Another application example is the realisation of III-As and III-Sb nanowires and finfets for low power logic applications using a lateral ALE process to minimize the wire diameter and fin width. A further example is using a lateral ALE process to selectively etch gate metal stacks to form nanometer scale T-gates required for low noise for RF devices (Fig 3). This has been achieved using Si industry compatible subtractive processes and without the need for complicated resist stacks.

In our ALE processes, Cl_2, HBr, and SF_6 have been used as the reactive gases for surface modification, with the details depending on the etched materials and target applications. The etching chemistries are based on the formation of self-limited Ga, In, Al, and Sb halides in the case of III-V materials or Mo, W and Pt in the case of T-gate metal stacks. The modified surfaces are then removed using an Ar plasma formed with optimized RF and/or ICP power. The impact of all ALE process parameters on etch induced electrical damage has been an important aspect of our work (Fig 4)

To gain insight into the etching mechanisms, in-situ surface analyses have been carried out using Auger spectrometry and XPS techniques. The ALE processes and surface analyses which will be described in this presentation are carried out in a cluster tool from Oxford Instrument Plasma Technology, which includes an ICP etching chamber with repeat loop function and a Scienta Omicron NanoSAM surface analysis tool with Auger spectrometer and XPS (Fig 1). The clustered arrangement enables samples to be subjected to plasma processing and then transferred, under vacuum, into the analysis chamber. This flexibility enables each step of the ALE cycle to be evaluated (Figs 5&6).

4:30pm **ALE2-MoA-13 GaN and Ga_2O_3 Thermal Atomic Layer Etching Using Sequential Surface Reactions***, N Johnson, Y Lee,* ***Steven M. George,*** University of Colorado - Boulder

Atomic layer etching (ALE) of GaN and Ga_2O_3 is important for the fabrication of power electronics devices. Thermal ALE of GaN and Ga_2O_3 was performed using sequential, self-limiting surface reactions. The thermal ALE was accomplished using fluorination and ligand-exchange reactions. XeF_2 and HF were used as the fluorination reactants. BCl_3 was the main metal precursor for ligand-exchange. Ga_2O_3 was also etched using $Al(CH_3)_3$, $AlCl(CH_3)_2$, $TiCl_4$ or $Ga(N(CH_3)_2)_3$ as the metal precursors for ligand-exchange.

Crystalline GaN samples prepared using MOCVD techniques were etched with sequential XeF_2 and BCl_3 exposures. GaN etch rates varied from 0.18 to 0.72 Å/cycle at temperatures from 170 to 300°C, respectively (see Supplemental Figure 1). Because the GaN etch rates were self-limiting versus BCl_3 exposure and BCl_3 pressure, the GaN etching mechanism is believed to involve XeF_2 fluorination of GaN to GaF_3 and then ligand-exchange between BCl_3 and GaF_3 to yield volatile BCl_wF_x and GaF_yCl_z species. GaN fluorination using a NF_3 plasma was also successful for etching crystalline GaN at 250°C.

Ga_2O_3 samples deposited using ALD techniques were etched with sequential HF and BCl_3 exposures. Ga_2O_3 etch rates varied from 0.59 to 1.35 Å/cycle at temperatures from 150 to 200°C, respectively. The Ga_2O_3 etch rates were self-limiting versus HF and BCl_3 exposure. Ga_2O_3 ALE was also performed using HF for fluorination and a variety of metal precursors for ligand-exchange. Ga_2O_3 etch rates at 250°C were 0.2, 0.8, 1.1 and 1.2 Å/cycle for $Ga(N(CH_3)_2)_3$, $TiCl_4$, $Al(CH_3)_3$ and $AlCl(CH_3)_2$ as the metal precursors, respectively (see Supplemental Figure 2). The wide range of metal precursors that can etch Ga_2O_3 argues that the ligand-exchange reaction with GaF_3 is facile

4:45pm **ALE2-MoA-14 Selective GaN Etching Process using Self-limiting Cyclic Approach for Power Device Applications***,* ***Frédéric Le Roux,*** *N Posseme, P Burtin, S Barnola, A Torres,* Univ. Grenoble Alpes, CEA, LETI, France

Formation of the two-dimensional electron gas (2DEG) in AlGaN/GaN heterostructrures is the key-point for successful development of GaN-based power-electronics such as High Electron Mobility Transistors (HEMT) and diodes. Plasma-etching steps are considered as critical in fabrication for such devices. Indeed standard chlorine plasma[1] can lead to surface roughness degradation[2] and surface state modifications (non-stoichiometric layers, surface potential modifications and dangling bonds)[3–5]. This is why Atomic Layer Etching (ALE) and Digital Etching (DE) are developed to limit the material degradations and to have a better etch depth control[6]. The aim of this study is first to evaluate a self-limited GaN etching process using DE for power devices. This DE consists in two steps. First an O_2 plasma oxidizes the GaN surface. Then, the oxidized layer is removed using BCl_3 plasma selectively to the non-oxidized GaN.

Experiments have been carried out on 200mm wafer using the following stack: GaN (80 or 20nm)/$Al_{0,22}Ga_{0,78}N$ (24nm)/AlN (<1nm)/GaN (1,8µm)/buffer layers/Si substrate.

The development and optimization of the DE process will be presented. The etch mechanism of the self-limited process has first been understood thanks to XPS analyses performed on blanket wafers. It will be demonstrated that the O_2 plasma oxidizes the surface until a saturation level, which enable the self-limitation. Then the BCl_3 plasma removes the oxidized film selectively to the non-oxidized GaN film. This selectivity has been explained by the deposition of B_xCl_y layer on non-oxidized GaN. Small amount of boron oxide by-products is also detected at on the surface after the DE.

Then DE O_2/BCl_3 cyclic process has been compared to standard chlorine based plasma. It will be shown that the roughness and the uniformity are similar for both processes, while the cyclic process present better performances in term of electrical and material degradation. The benefit of the self-limited GaN etching process has finally been validated on patterned wafers for power device integration.

In the second part of this study, the first results of a Cl_2/Ar ALE process for GaN etching will be presented and compared to the DE O_2/BCl_3 cyclic process.

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5:00pm **ALE2-MoA-15 ALE of GaN (0001) by Sequential Oxidation and H_2/N_2 Plasma***,* ***Kevin Hatch****, D Messina, H Fu, K Fu, X Wang, M Hao, Y Zhao, R Nemanich,* Arizona State University

Atomic layer etching of GaN may be used to reduce the high surface defect concentrations produced during inductively coupled plasma (ICP) etching and other processing methods. We have demonstrated a new method for plasma enhanced atomic layer etching (PEALE) of GaN (0001) using sequential surface modification by remote O_2 plasma, followed by removal of the surface oxide through H_2/N_2 plasma etching. The efficacy of etching the surface oxide via H_2/N_2 plasma exposure was confirmed by deposition and removal of several nm of plasma enhanced atomic layer deposited (PEALD) Ga_2O_3 epilayers on GaN. The composition of the H_2/N_2 plasma was investigated, and a H_2:N_2 volumetric flow ratio of 2:1 was found to produce sufficient etch rates at 500°C. An etch per cycle (EPC) of 2 nm was achieved and is attributed to the oxidation rate of GaN. This PEALE process was performed on “as-grown” unintentionally doped GaN (UID-GaN) deposited on a GaN substrate by metalorganic chemical vapor deposition (MOCVD), which also underwent $Ar/Cl_2/BCl_3$ ICP etching prior to the PEALE process. Application of several PEALE cycles resulted in improved surface stoichiometry, which was attributed to removal of Ga-rich layers created during ICP etching. After the PEALE process the N:Ga ratio increased from 0.5 to 0.8, and the surface roughness improved from R_{RMS} = 0.3 nm to R_{RMS} = 0.2 nm, as measured by AFM. This ALE process has been performed on ICP etched samples prior to regrowth and the I-V characteristics have been measured, showing improved voltage breakdown observed.

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5:15pm **ALE2-MoA-16 Comparative Study of Two Atomic Layer Etching Processes for GaN***,* ***Cédric Mannequin****, C You,* University of Tsukuba, Japan*; G Jacopin, T Chevolleau, C Durand,* University Grenoble-Alpes, France*; C Vallée,* LTM-UGA, France*; C Dussarat, T Teramoto,* Air Liquide Laboratories, Japan*; H Mariette,* University Grenoble-Alpes, France*; K Akimoto, M Sasaki,* University of Tsukuba, Japan*; E Gheeraert,* University Grenoble-Alpes, France

Drastic reduction of defect density after etching in nitride semiconductor-based devices becomes a pressing requirement to improve further device performances. Defects introduced by etching process during the formation of the recess gate at AlGaN/GaN or during the fabrication process of GaN displays based on µ-Light Emission Diodes are the main sources issues of devices reliability degradation. Atomic Layer Etching (ALE) processes relying on two times separated half reactions: adsorption step and activation step are of great interests for solving these issues.

In this work, we propose a comparative study of two ALE processes for undoped *c*-oriented Ga-polar GaN, relying both on Cl_2-based plasma for the absorption step but using two different gases for the activation step. The two ALE processes were developed in an Inductively Coupled Plasma etcher (RIE-200iP from SAMCO). In-situ Optical Emission Spectroscopy (OES) was used to monitor gas dissociation for the adsorption, activation and purge steps, allowing identification of active species. Additionally, OES monitoring were used to calibrate Cl_2 dosing time and purging time to ensure complete separation of the Cl_2 dissociation by-products and the gas used for the activation step. The ICP source power (RF_{source}) and pressure for the adsorption step were varied in the 5—120 W range and 0.65—2 Pa range, respectively. For set adsorption step conditions, the self-bias (V_{DC}) of the activation step was varied in the range of 11—40 V by changing the ICP Bias power (RF_{bias}). For each condition, the Etching rate Per Cycle (EPC) was estimated from the etched depth of GaN submitted to 200 ALE cycles using

Scanning Electron Microscopy images and reported as a function of V_{DC} (from the activation step).

In the case of the first activation gas, we report an ALE mode with an EPC of 0.276 nm, corresponding to 1.3 monolayer (ML) of the GaN wurtzite structure in the *c*-direction. For this first activation gas, a constant EPC were observed for V_{DC} in the 15—17 V range consistent with ALE process. For higher V_{DC}, the EPC continuously increase with V_{DC}. For the second activation gas, we report an ALE mode presenting an EPC of 0.567 nm corresponding to 2 ML. A constant EPC for V_{DC} in the 16—22 V range were observed. From Atomic Force Microscopy observations of 500 x 500 nm^2, we report significant decrease of the Rms roughness from 0.18 nm for as-deposited GaN surface to 0.07 nm after ALE processing.

Finally, we will discuss and tentatively propose mechanisms to explain the significant differences observed between our two ALE approaches.

5:30pm **ALE2-MoA-17 Chlorinated Surface Layer of GaN in Quasi Atomic Layer Etching of Cyclic Processes of Chlorine Adsorption and Ion Irradiation***,*
Masaki Hasegawa*, T Tsutsumi,* Nagoya University, Japan*; A Tanide,* SCREEN Holdings Co., Ltd.*; H Kondo, M Sekine, K Ishikawa, M Hori,* Nagoya University, Japan

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

Samples were GaN films grown on sapphire substrate by Hydride Vapor Phase Epitaxy (HVPE) method. Prior to the beam experiments, native oxide on GaN surface was removed by wet cleaning (5% HF) and Ar ion sputter. The as-cleaned surface was exposed by Cl radicals with a dosage of 10^{19} cm^{-2} generated in Cl_2 gas (flow rate 0.5 sccm) plasma by application of RF power of 400 W. Next, Ar ions with a dosage of 10^{16} cm^{-2} and the accelerating voltage of 100 V or 200 V. The one cycle consisted of these Ar ion irradiation and Cl radical exposure. To stabilize the GaN surface, five cyclic processes were carried out. Then, the GaN surface at each step was analyzed by angle-resolved XPS with take-off-angles of 20, 30, 40, 60, and 90 degrees with respect to the wafer plane. Depth profiles were analyzed by the maximum entropy method.

The Ar ion bombardments change the GaN surface to Ga-rich. Subsequently, as the ion-bombarded Ga-rich surface exposes to the Cl adsorption step, the surface stoichiometry recovers to high N/Ga ratio, resulting to form Ga chlorides as a volatile. The depth profiles obtained from XPS data after the 7th Cl radical exposure were compared with the different Ar ion energies. In the depth profiles of Cl concentration after Cl radical exposure after irradiation with 100-eV-ion (a) and 200-eV-ion (b), the Cl amount and penetration with a depth of approximately 2 nm during the Cl radical exposure were in details observed quantitatively. In the Ar ion bombardments, the formation of non-bonded Ga (dangling bond) and disordered structure was dominated by the ion energies. The resultant etching depth per cycle and the surface stoichiometry were depended on the non-bonded Ga amounts that resulted to desorb Ga chlorides during the Cl radical exposure. This indicates that the surface chlorination layer determined the ALE-properties of real layer-by-layer etching and self-limiting reaction. Not only the ion energy but also the chlorination layer depths should be taken account for the ALE cyclic processes.

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Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE1-TuM
ALE: Gas-phase and/or Thermal ALE

Moderators: Steven M. George, University of Colorado at Boulder, Venkateswara Pallem, AirLiquide

8:00am **ALE1-TuM-1 Analyses of Hexafluoroacetylacetone (Hfac) Adsorbed on Transition Metal Surfaces***, **Tomoko Ito**, K Karahashi, S Hamaguchi,* Osaka University, Japan **INVITED**

Transition metals are known as hard-to-etch materials for reactive ion etching (RIE) processes. Although Ar milling processes are now widely used for such metal etching, physical sputtering processes with high energy ions have problems of low selectivity and poorly controlled etched profiles. Surface damages induced by energetic ion bombardment may also cause degradation of the material surface properties. Therefore alternative transition-metal etching processes with high selectivity and low damage, rather than physical sputtering, have been sought after in the industry. In recent years, atomic layer etching (ALE) by the formations of volatile organic metal complexes has attracted much attention as a means to achieve atomically controlled and low damage etching. ALE reactions may be considered as reverse reactions of atomic layer deposition (ALD). For example, metal beta-ketoenolate complexes are often used as precursors for ALD, so stable adsorption of beta-ketones on a metal surface and the formation of metal beta-ketoenolates thereon are crucial steps for the development of corresponding ALE processes. In this study, we have examined surface reactions of transition metals or their oxides with hexafluoroacetylacetone (hfac) [1] and demonstrated that such reactions can be used to develop ALE processes for some transition metals. Experiments were performed in what we call the "Atomic-Layer-Process (ALP) Surface Analysis System," which consists of ALP reaction chambers and an *in-situ* high-resolution X-ray photoelectron spectroscopy (XPS) system. In the reaction chamber, the substrate temperature can be controlled by a ceramic heater, which is installed on the back side of the sample. After exposure to reactive gases, the sample can be transferred from the reaction chamber to the XPS chamber without being exposed to ambient air for *in- situ* surface chemical analysis. Ion irradiation effects on an hfac adsorbed metal surface may be studied with the use of low energy Ar^+ ion beam of the XPS system. We used Ni and Co substrates in this study. It has been found that hfac molecules adsorbed on a metal oxide surface are less likely to be decomposed at room temperature than those on a metal surface and, at an elevated temperature, a metal oxide surface is preferentially etched by hfac than a metal surface.

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8:30am **ALE1-TuM-3 Thermal Atomic Layer Etching of Silicon Nitride using an Oxidation and "Conversion-Etch" Mechanism***, **Aziz Abdulagatov**, S George,* University of Colorado - Boulder

The thermal atomic layer etching (ALE) of silicon nitride was demonstrated using an oxidation and "conversion-etch" mechanism (see Supplemental Figure 1). In this process, the silicon nitride surface was oxidized to a silicon oxide layer using O_2 or ozone. The silicon oxide layer was converted to an Al_2O_3 layer using trimethylaluminum (TMA). The Al_2O_3 layer was fluorinated by HF to an AlF_3 layer prior to the removal of the AlF_3 layer by ligand-exchange using TMA. Silicon nitride ALE was studied using Si_3N_4 films deposited using low pressure chemical vapor deposition (LPCVD). *In situ* spectroscopic ellipsometry was employed to monitor the thickness of both the Si_3N_4 and the silicon oxide layer during ALE. These studies observed that the silicon nitride film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant.

Using an O_2-HF-TMA reaction sequence, the Si_3N_4 ALE etch rate was 0.26 Å/cycle at 290°C. This etch rate was obtained using static reactant pressures of 250, 0.65 and 1.0 Torr, and exposure times of 10, 5 and 5 s, for O_2, HF and TMA, respectively. Employing similar dosing conditions, the process using O_3 yielded a higher Si_3N_4 etch rate of 0.47 Å/cycle (see Supplemental Figure 2). The Si_3N_4 etch rates remained the same for O_3 pressures from 30-250 Torr. The order of the reactant sequence affected the Si_3N_4 etch rate. Changing the reactant sequence from O_3-HF-TMA to O_3-TMA-HF reduced the Si_3N_4 etch rate from 0.47 to 0.20 Å/cycle at 290°C. The Si_3N_4 ALE etch rate was also reduced at lower temperatures. Using the O_3-HF-TMA reaction sequence, the Si_3N_4 etch rate was reduced from 0.47 Å/cycle at 290°C to 0.07 Å/cycle at 210°C.

Si_3N_4 ALE also decreased the roughness of the Si_3N_4 surface. The RMS roughness of the initial Si_3N_4 films was 4.7 Å measured using atomic force microscopy (AFM). The RMS roughness decreased to 3.1 Å after 80 ALE cycles. An SiO_2 oxide thickness of ~10-15 Å remained after Si_3N_4 ALE at 290°C. This oxide could be removed by 15 sequential TMA and HF exposures after the Si_3N_4 ALE. Thermal Si_3N_4 ALE should be useful in advanced semiconductor fabrication. Thermal Si_3N_4 ALE could also find applications in optoelectronics, photonics and MEMS fabrication.

8:45am **ALE1-TuM-4 Thermal Dry Atomic Layer Etching of Cobalt with Sequential Exposure to Molecular Chlorine and Diketones***, M Konh, C He, X Lin,* University of Delaware*; X Guo, V Pallem,* American Air Liquide*; R Opila, **Andrew Teplyakov**, Z Wang, B Yuan,* University of Delaware

The mechanism of thermal dry etching of cobalt films is discussed for a thermal process and a sequential exposure to chlorine gas and a diketone (either 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfacH) or 2,4-pentanedione (acetylacetone, acacH)). The process can be optimized experimentally to approach atomic layer etching (ALE), and a sequential exposure to Cl_2 and hfacH dry etchants at 140°C is shown to proceed efficiently. The use of acacH as a diketone does not result in ALE with chlorine even at 180°C; however, the decrease of surface chlorine concentration and chemical reduction of cobalt is noted. Thermal desorption analysis suggests that the reaction of chlorinated cobalt surface exposed to the ambient conditions (oxidized) with hfacH does produce volatile Co-containing products within the desired temperature range and the products contain Co^{3+}. The effect of ligands on the energy required to remove surface cobalt atoms is evaluated using density functional theory and the findings are consistent with the experimental observation of surface smoothing during atomic layer etching.

9:00am **ALE1-TuM-5 Spontaneous Etching of B_2O_3 and TiO_2 by HF: Removal Reaction in WO_3 ALE and TiN ALE***, **Austin Cano**,* University of Colorado - Boulder*; S Natarajan,* Tyndall National Institute, Ireland*; J Clancey,* University of Colorado - Boulder*; S Elliot,* Schrödinger Inc*; S George,* University of Colorado - Boulder

Thermal atomic layer etching is typically based on two sequential surface reactions. The first reaction activates the surface layer and the second reaction leads to material removal by the desorption of volatile etch products. The surface activation can be halogenation, conversion to a different material, or oxidation of the initial material. For example, BCl_3 is able to convert the WO_3 surface to a B_2O_3 surface layer during WO_3 ALE. The B_2O_3 surface layer is then spontaneously removed by etching using HF. In another example, O_3 is able to oxidize the TiN surface to a TiO_2 surface layer during TiN ALE. The TiO_2 surface layer is then spontaneously removed by etching using HF.

This study explored the spontaneous etching of B_2O_3 and TiO_2 with HF using Fourier Transform Infrared (FTIR) spectroscopy and quadrupole mass spectrometry (QMS) analysis. The initial B_2O_3 films were grown using B_2O_3 ALD with BCl_3 and H_2O as the reactants. The initial TiO_2 films were grown using TiO_2 ALD with $TiCl_4$ and H_2O as the reactants. FTIR measurements observed the growth of the B_2O_3 films and TiO_2 films by monitoring the absorbance of the B-O and Ti-O stretching vibrations, respectively, versus number of ALD cycles. FTIR experiments also observed the spontaneous etching of B_2O_3 and TiO_2 with HF by measuring the loss of the absorbance of the B-O and Ti-O stretching vibrations, respectively (See Supplemental Figure 1).

QMS studies were also able to monitor the volatile etch products during the spontaneous etching of B_2O_3 nanopowder with HF. The expected reaction products are BF_3 and H_2O based on the reaction $B_2O_3 + 6HF \rightarrow 2BF_3 + 3H_2O$. In comparison, the QMS detected $B(OH)F_2$, BF_3 and H_2O as the main etch products (See Supplemental Figure 2). In addition, the QMS also revealed species at higher masses that were consistent with six-member ring species, such as $B_3O_3F_3$.

The reaction of HF with B_2O_3 and TiO_2 was also examined using a density functional theory (DFT) based computational approach. By comparing the thermodynamic free energy profiles of competing self-limiting surface and bulk reactions, the DFT calculations predicted the spontaneous etching of B_2O_3 by HF above -160°C and of TiO_2 (but not TiN) above 90°C, in agreement with the experimental findings.

9:15am **ALE1-TuM-6 Thermal Based Atomic Layer Etching of Aluminum Oxide and Titanium Nitride***, **Varun Sharma**, T Blomberg, M Tuominen, S Haukka,* ASM, Finland

Thermal based Atomic Layer Etching (th-ALEt) has opened a new horizon and triggered an increased interest in the Semiconductor Industry for the

fabrication of sub-10 nm as well as complex 3D nano-devices. In the th-ALEt technique, a material is chemically etched from thermally activated surface by sequence of one or more reactants each separated by purge steps. Unlike the conventional anisotropic plasma etching, th-ALEt is isotropic, selective and its slow etch rate may possess excellent atomic-scale control. Most of the reported th-ALEt chemistries utilize hydrogen fluoride (HF from HF-pyridine) as one of the reactants. However, due to some safety concerns associated with the use and handling of HF, we have considered other fluorine donating compounds. In this work, we report niobium pentafluoride (NbF_5) as an alternative to HF. Carbon tetrachloride (CCl_4) is used as a co-reactant with NbF_5 to etch aluminum oxide (Al_2O_3) as well as titanium nitride (TiN). The various attributes of the etching process like etch rates, selectivity and post-etch surface roughness were studied. It was found that NbF_5 promotes the fluorination of Al_2O_3 and the fluorinated Al_2O_3 surface can be etched away by a subsequent exposure of CCl_4 gas. TiN can be etched in continuous pulsed mode just by CCl_4, while adding NbF_5 to the process enables etch-rate control. The etch results and proposed reaction pathway for the etching of Al_2O_3 and TiN will be discussed in the presentation.

9:30am **ALE1-TuM-7 Thermal Atomic Layer Etching of Amorphous and Crystalline Hafnium Oxide, Zirconium Oxide and Hafnium Zirconium Oxide*, Jessica A. Murdzek*,** *S George,* University of Colorado - Boulder

Thermal atomic layer etching (ALE) can be achieved with sequential surface reactions using the fluorination and ligand-exchange mechanism. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming volatile products. Previous studies have demonstrated the thermal ALE of amorphous HfO_2 and ZrO_2 ALD films. No previous investigations have explored the differences between the thermal ALE of amorphous and crystalline films. The thermal ALE of crystalline films is important because amorphous films may not crystallize easily when they are too thin. Consequently, amorphous films may have to be grown thicker, crystallized, and then etched back to obtain the desired ultrathin crystalline film thickness.

This study explored the thermal ALE of amorphous and polycrystalline films of hafnium oxide, zirconium oxide, and hafnium zirconium oxide. HF was used as the fluorination reactant. Dimethylaluminum chloride (DMAC) or titanium tetrachloride was employed as the metal precursor for ligand-exchange. The amorphous films had a much higher etch rate per cycle than the crystalline films. The differences were most pronounced for hafnium oxide. At 250 °C with HF and DMAC as the reactants, the etch rate was 0.03-0.08 Å/cycle for crystalline HfO_2 and 0.68 Å/cycle for amorphous HfO_2 (See Supplemental Figure 1).

Under the same conditions at 250 °C with HF and DMAC as the reactants, the etch rate was 0.60-0.82 Å/cycle for crystalline ZrO_2 and 1.11 Å/cycle for amorphous ZrO_2. In comparison, the etch rate was 0.16-0.26 Å/cycle for crystalline $HfZrO_4$ and 0.69 Å/cycle for amorphous $HfZrO_4$. The etch rates for $HfZrO_4$ were between HfO_2 and ZrO_2 for both the amorphous and crystalline films. When HF and $TiCl_4$ were used as the reactants at 250 °C, the etch rates were smaller than the etch rates with HF and DMAC as the reactants for every material. The etch rates also increased with temperature for both the amorphous and crystalline films. The differences between amorphous and crystalline HfO_2 are sufficient to obtain selective thermal ALE of amorphous HfO_2.

9:45am **ALE1-TuM-8 Isotropic Atomic Layer Etching of Cobalt with Smooth Etched Surfaces by using Cyclic Repetition of Plasma Oxidation and Organometallization*, Sumiko Fujisaki,*** Hitachi R&D Group, Japan

Isotropic atomic layer etching (ALE), which produces atomically precise, conformal removal, will have an important role in semiconductor manufacturing. This is because highly selective ALE has become necessary to deal with processing of new materials with the advances in minitualization of devices such as 3D structures. In the past several years, isotropic ALE of various materials has been reported which includes thermal ALE for metal oxides and thermal-cyclic ALE for nitride films [1]. To meet the requirements concertning the variety of materials to be etched, isotropic ALE of cobalt must be developed. In 2018, thermal ALE of cobalt has been reported by using treatment with formic acid and ligands to produce volatile cobalt complexes [2]. In this paper, the authors successfully demonstrate isotropic ALE of cobalt film with smooth etched surfaces, which is important issue in the development of ALE of cobalt.

The experimental apparatus used in this study is 300-mm ALE tool equipped with inductively-coupled plasma source and infrared lamps. The cyclic ALE process is composed of three step repetitions: oxidation of cobalt surface with oxygen plasma, organometallization of the cobalt oxide with a low acidity ligand vapor, and sublimation of the organemetallic cobalt by thermal annealing.

The etching depth of cobalt increased with increasing the number of repetitions of the cycle. For one cycle of etching, it was 1 nm high. The root-mean-square (RMS) roughness of etched cobalt surface was estimated to be 0.8 nm. It was found that formation of homogeneous CoO (II) was important because compound oxide such as Co_3O_4 (II & III) resulted in rough etched surfaces with columnar morphology. Furthermore, controllability of etching amount was substantially improved by using low reactivity ligands compared to high-reactivity ligands. These results implied that the combination of homogenious CoO formation, low-reactivity ligands, and sublimation was essential for achieving smooth etched surfaces and excellent controllability of etching amount.

In conclusion, we have obtained well-controlled etch front roughness and etching depth of cobalt, which can be applied to semiconductor process, by controlling reactions of both oxidation and metal complex formation using the 300-mm ALE apparatus.

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

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

Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE2-TuM
Alternative Methods to ALE

Moderators: Jean-François de Marneffe, IMEC, Satoshi Hamaguchi, Osaka University, Japan

10:45am **ALE2-TuM-12 Atomic Layer Etching for Germanium using Halogen Neutral Beam =Comparison between Br and Cl Chemistry=**, *T Fujii,* ***Daisuke Ohori,*** Tohoku University, Japan*; S Noda,* National Institute of Advanced Industrial Science and Technology, Japan*; Y Tanimoto, D Sato, H Kurihara,* Showa Denko K.k.*; W Mizubayashi, K Endo,* National Institute of Advanced Industrial Science and Technology, Japan*; Y Li,* National Chiao Tung University*; Y Lee,* National Nano Device Laboratories*; T Ozaki, S Samukawa,* Tohoku University, Japan

Recently, 3D Fin field-effect transistors (FETs) have been developed for breaking through limitations of the short-channel effect for highly scaled metal-oxide-semiconductor (MOS) FETs. However, the Ge channel formation for Fin FET has not been deeply investigated since the Ge etching reaction is not known well compared to the Si etching reaction. As a result, the carrier mobility degradation was observed by electron scattering due to surface roughness and defects on the channel sidewall surface etched by conventional plasma etching (PE). In the PE, energetic ion bombardment and ultraviolet (UV) light irradiation cause a large side-etching, sidewall surface defects, and sidewall surface roughness. These lead to the degradation of carrier mobility and I-V characteristics [1]. To realize higher performance electrical characteristics without compromising the intrinsic high carrier mobility of Ge, atomic layer defect-free, roughness-free, and profile-controlled etching must be accomplished for future sub-10 nm Ge Fin FET. In this work, we demonstrated atomically flat, extremely high selective and defect-free etching with the hydrogen bromide (HBr) neutral beam etching, and investigated the mechanism compared with the Cl_2 NBE.

We investigated Ge etching rate dependence on the substrate temperature from -20 to 150 ºC by using HBr and Cl_2 neutral beam. Sample structure was p-type Ge (100) wafer with SiO_2 line pattern mask of 150 nm in width of a nanoimprint.

We carried out the cross-sectional SEM observation and ellipsometer measurement for checking the Ge etching rate and SiO_2 etching rate, respectively. For the HBr NBE, the Ge etching rate was almost constant at 35 nm/min from -20 to 90 ºC. On the other hand, for the Cl_2 NBE, the Ge etching rate linearly increased from 38 to 45 nm/min from -20 to 150 ºC. SiO_2 etching rate for HBr and Cl_2 NBE were 0.3 nm/min and 2.8 nm/min at any substrate temperature, respectively. The HBr NBE could realize almost 10 times higher etching selectivity as compared with Cl_2 NBE. Moreover, the sidewall etching for HBr NBE was perfectly eliminated from -20 to 90 ºC. In contrast, the sidewall etching for Cl_2 NBE occurred at more than 90 ºC. It is considered that non-volatile Bromide protected layer, such as $GeBr_4$ and $Si_xBr_yO_z$was formed on the Ge sidewall and SiO_2 top surface in case of using HBr. HBr NBE could perfectly eliminate the sidewall etching and obtain extremely high etching selectivity to SiO_2 even at more than 90 ºC . In conclusion, we succeeded to fabricate the Ge Fin structure of highly anisotropic and extremely high selectivity with HBr NBE.

[1] W. Mizubayashi, et al., Appl. Phys. Express, 10, 026501 (2017).

11:15am **ALE2-TuM-14 A New Etching / Passivation Process in Cyclic Mode for Spacer Etching in 3D CMOS Integrations***, O Pollet,* CEA-LETI, France*; N Posseme,* Univ. Grenoble Alpes, CEA, LETI, France*; V Ah-Leung,* ***Valentin Bacquie****,* CEA-LETI, France

With ever-decreasing gate length in CMOS technology, integrations have changed from planar to 3D architectures, such as FinFET or stacked nanowires, where the channel is a tall and narrow structure protruding from the surface, thereby providing a better electrostatic control and reduced leakage. However from an etch standpoint this raises new challenges particularly for spacer formation since the stopping layer has become a structured surface instead of being flat, which induces the formation of parasitic spacers on channel sidewalls. To overcome this issue overetch must be significatively lengthened, from 30-50% in planar CMOS to 200-300% in 3D CMOS. Considering other requirements such as no CD loss, no channel material loss or damaging, spacer etching has turned into a very challenging process.

Conventional processes based on fluorocarbon chemistries like $CH_3F/CH_4/O_2$ do not provide sufficient selectivity to silicon to enable long overetch required to get rid of spacers on channel sidewalls without considerably consuming or damaging the channel material. To improve selectivity a new process was proposed recently, that contains $SiCl_4$ in addition to fluorocarbon in the etching chemistry.

XPS analyses showed that this specific gas composition leads to the deposition of SiO_xF_y, which acts as a passivation layer on silicon, instead of the usual carbon-rich organic film deposited with CH_zF_w/O_2 chemistries. Ellipsometry measurements highlighted that SiO_xF_y passivation grows preferentially on silicon than on silicon nitride, which allows etching to carry on this material while silicon is passivated. Less than 1nm of silicon consumption is consistently measured even for long process times while at the same time silicon nitride is etched linearly providing a selectivity up to 40:1 between nitride and silicon.

To further improve process performance this $SiCl_4$-containing process was combined in a cyclic mode with a non-selective CHF_3 step. The $SiCl_4$ step function is to etch silicon nitride while depositing passivation on silicon. During the CHF_3 step both silicon nitride and passivation on silicon are etched and respective step times were set up in such way that silicon nitride is linearly etched at a rate of 7.3nm/cycle while the silicon surface is permanently covered by the SiO_xF_y layer. This ALE-inspired process was demonstrated on a stacked nanowires integration: a 12.5nm thick SiN IRAD spacer was etched with very limited CD bias on the gate while parasitic spacers formed on 36nm high active area sidewalls were thoroughly removed without inducing more than 1.5nm silicon consumption.

11:30am **ALE2-TuM-15 Atomic Layer Etching of Transition Metals with Gas Cluster Ion Beam Irradiation and Acetylacetone***,* ***Noriaki Toyoda****, K Uematsu,* University of Hyogo, Japan

Atomic layer etchings (ALE) of transition metals with gas cluster ion beam (GCIB) and acetylacetone were investigated. In general, the ion energy in the removal step in ALE is several tens of eV, which is higher than the sublimation energy of the surface layer (several eV). These excess energies might be the origin of the damages on the target materials. We have investigated the feasibility of GCIB as energetic ions in the removal steps of ALE process. Since GCIBs are aggregates of thousands of gas atoms or molecules, the energy/atoms or energy/molecules can be easily reduced to several eV even though the total energy of GCIB is several keV. In additions, since GCIB induce dense energy deposition without severe damage, the bombarded area experiences transient high-temperature and high-pressure conditions. As a result, chemical reactions are enhanced at low-temperature. In the previous study, ALE of Cu films was demonstrated successfully using O_2-GCIB and acetic acid.

In this study, we have investigated ALE process for transition metals (Cu and Ni) using acetylacetone. We separated each etching step as following; (1) adsorption of acetylacetone on metal oxide, (2) evacuation of residual acetylacetone vapor, (3) irradiation of O_2-GCIB to remove metal oxide. Effects of the following etching parameters on ALE were investigated from real-time thickness on a quartz crystal monitor; acceleration voltage of oxygen GCIB, irradiation time of GCIB, exposure time of acetylacetone.

When the acceleration voltage of O_2-GCIB is 20 kV, very thin layer of nickel oxide with adsorbed acetylacetone is removed quickly, however, Ni atoms are physically sputtered. Consequently, the etching process with 20 kV oxygen GCIB is not self-limiting. On the contrary, surface nickel oxide with adsorbed acetylacetone are removed by 5 kV O_2-GCIB and there is no physical sputtering. Since the average cluster size of O_2-GCIB is 3000 molecules/ion, the energy/molecule is below 2 eV. By using 5 kV O_2-GCIB, self-limiting removal step is realized.

11:45am **ALE2-TuM-16 Atomic Layer Etching at Atmospheric Pressure***,* ***Eugen Shkura****, D Theirich, K Brinkmann, T Haeger,* University of Wuppertal, Germany*; J Schneidewind, M Siebert,* SENTECH Instruments GmbH, Germany*; T Riedl,* University of Wuppertal, Germany

Atomic Layer Etching (ALE) is a cyclic process which is based on sequential surface reaction of two or more reactants and ideally provides control on the monolayer level. In the last decade the main focus was on two types of ALE. The first approach relies on the chlorination and sometimes fluorination to initially create metal-halide species at the surface which are subsequently removed by a plasma [1,2]. Another approach is thermally driven ALE, e.g. by using HF and $Sn(acac)_2$ to etch metal oxides [3]. More recent reports indicated isotropic etching by using radically driven, plasma enhanced ALE [4]. In all these examples, the ALE process is vacuum based and as such provides some limitations towards high throughput and low manufacturing costs. Here, we introduce a novel process for Atomic Layer Etching at atmospheric pressure (AP-ALE). As a case study, we investigate the etching of ZnO by AP-ALE and spatial AP plasma enhanced-ALE by using Hacac at substrate temperatures in the range of 80-140 °C. Ozone as well as an atmospheric pressure dielectric Ar/O_2 barrier discharge is used for AP-ALE and spatial AP Plasma Enhanced-ALE, respectively. In-situ quartz crystal microbalance as well as ex-situ spectroscopic ellipsometry were used to characterize the etching process. Depending on the processing conditions, an etch per cycle of 0.5 to 5 Å is found. Ex-situ AFM measurements before and after ALE show a modification of ZnO-Surface and a decrease in film thickness. Furthermore, growth characteristics in dependence of process parameters like substrate velocity and substrate temperature were investigated. We discuss the prospects to use spatial AP-ALE for materials other than metal oxides, such as III-V semiconductors like GaN or AlGaN.

[1] K.J. Kanarik et al. Solid State Technology 56(8) 14-17 (2013).

[2] S. Rauf et al. J. Appl. Phys. 101, 033308 (2007).

[3] Y. Lee et al., ACS nano, 9(2), 2061-2070. (2015).

[4] A. Mameli et al., ACS Applied Mater. & Interfaces 10, 38588-38595 (2018).

Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE1-TuA
Modeling & Instrumentation I

Moderators: Ankur Agarwal, KLA-Tencor, Alok Ranjan, TEL Technology Center, America, LLC

1:30pm **ALE1-TuA-1 Atomic Layer Etching of Nanostructures***, **Sabbir Khan**,* Niels Bohr Institute, University of Copenhagen, Denmark*; D Suyatin,* Lund University, Sweden*; J Sundqvist,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany **INVITED**

Progress in modern electronics demands atomic precision-controlled fabrication of devices and atomic layer etching (ALE) provides etch processes which can assist device trimming with atomic precision. ALE is now becoming a key technique for nanofabrication and the semiconductor industry. In this talk we will demonstrate ALE of thin film Ga-polar GaN (0001) where surface modification is done by Cl_2 adsorption and later modified chlorinated layer is removed by low energy Ar ions in plasma environment using standard reactive ion etching (RIE) system (Oxford Plasmalab 100) [1]. Further, using a similar system, Cl_2 and Ar based highly anisotropic ALE on crystalline Si (100) with good etch selectivity for SiO_2 masks will be discussed. This high material selectivity enables nano-patterning of different geometries on Si wafer and post-ALE patterns inspection allows us to understand different effects (such as, trenching and sidewall tapering etc.) and limitations of the process. We also demonstrate that the ALE processed patterned substrates can be used as molds for high resolution nanoimprinting of features size down to 30 nm [2]. Finally, ALE on semiconductor nanowires will be shown, indicating that the process can be used for damage free processing of semiconductor nanowire devices and precise nanofabrication below 20 nm [3].

Reference:

1. Christoffer Kauppinen, Sabbir Ahmed Khan, Jonas Sundqvist, Dmitry B. Suyatin, Sami Suihkonen, Esko I. Kauppinen and Markku Sopanen. Atomic Layer Etching of Gallium Nitride (0001). Journal of Vacuum Science & Technology A, 35, 6, 060603 (2017).

2. Sabbir Khan, Dmitry B. Suyatin, Jonas Sundqvist, Mariusz Graczyk, Marcel Junige, Christoffer Kauppinen, Anders Kvennefors, Maria Huffman, Ivan Maximov. High-Definition Nanoimprint Stamp Fabrication by Atomic Layer Etching. ACS Applied Nano Materials, 1, 6, 2476–2482 (2018).

3. Sabbir Khan, Dmitry B. Suyatin, Jonas Sundqvist, A Method for Selective Etching of Nanostructures. WO2017157902A1, Patent Application (2017).

2:00pm **ALE1-TuA-3 Selectivity during Plasma ALE of Si-Compounds: Reaction Mechanism Studied by in-situ Surface Spectroscopy***, **René Vervuurt**,* ASM*; K Nakane, T Tsutsumi, M Hori, N Kobayashi,* Nagoya University, Japan

Plasma atomic layer etching (ALE) processes based on plasma modification and modification layer removal by fluorine radicals have recently been reported, for the etching of SiN and SiC [1-3]. The proposed processes offer advantages in terms of etch process control, uniformity and etch selectivity versus SiO_2 compared to more conventional etching techniques.

In this contribution the selective ALE of Si-compound films is investigated and the reaction mechanism behind the etch selectivity between compounds is discussed. H_2, He and N_2 plasma modification and the subsequent etching of the modified layer by F-radicals are studied by *in-situ* Fourier Transform Infrared Spectroscopy (FTIR) and spectroscopic ellipsometry (SE) for several Si-compounds (SiN, SiC, SiCOH, and SiO_2).

in-situ SE measurements show that the selectivity of the ALE process can be controlled by the modification plasma; H_2 plasma can be used for the selective etching of SiN, SiC and SiCOH versus SiO_2, whereas a N_2 plasma makes the selective etch of SiC and SiCOH versus SiN and SiO_2 possible. He plasma modification on the other hand did not result in etching by F-radicals.

The origin of the selectivity and underlying reaction mechanism is discussed on the basis of *in-situ* FTIR measurements. These show that H_2 plasma modification of SiN, creates a H-rich modification layer containing Si-H and N-H groups. Both Si-H and N-H group formation saturate with exposure time. The created Si-H and N-H groups are removed by the subsequent F-radical exposure resulting in the net removal of SiN. The reaction mechanism for H_2 plasma ALE of SiC and SiCOH is found to be similar; a H-rich layer is formed on top of the sample which can be etched using F-radicals, while SiO_2 is not modified. This makes it possible to selectively etch SiN, SiC and SiCOH versus SiO_2.

N_2 plasma can be used to selectively modify SiC versus SiO_2 and SiN by creating a Si-H and C=N rich layer. The Si-H groups are created by the restructuring of the hydrogen already present in the SiC film in the form of C-H bonds. The modified layer can be removed using F-radicals allowing for the selective etch of SiC.

He plasma exposure of SiN, SiC and SiCOH creates a Si-O rich modification layer. This layer cannot be removed by F-radicals and therefore does not result in etching.

The obtained results indicate that the formation of a Si-H rich layer is essential for the plasma ALE of SiN, SiC and SiCOH. By tuning the plasma conditions the formation of this layer can be controlled allowing for the selective ALE between SiN, SiC, SiCOH and SiO_2.

[1] Sherpa et al. *JVSTA* 35,1, 2016

[2] Kumakura et al. *DPS 2018*, Nagoya

[3] Vervuurt et al. *DPS 2018*, Nagoya

2:15pm **ALE1-TuA-4 Chamber Vacuum Strategies to Enable High Productivity ALE***, **Declan Scanlan**, D Stephenson, A Stover,* Edwards Vacuum, Ireland

As device lateral dimensions shrink with each successive technology node, the semiconductor industry is now poised to transition from the nanoscale era to the atomic scale era, and must now turn to atomic scale processing techniques.

Analogous to atomic layer deposition (ALD), Atomic Layer Etch is a technique for removing thin layers of material using sequential reaction steps that are either fully or quasi self-limiting. While this technique has shown extremely promising on-wafer results for a variety of etch applications, the transition into high volume manufacturing has been relatively restricted, since the productivity penalty, particularly wafer throughput, is still a major limiting factor. These sequential reaction steps typically require a full and complete exchange of the reactive gas chemistry within the chamber, and therefore a very high-flow, sequentially intermittent, gas purge step is often deployed. To improve the efficiency of this total gas exchange, equipment manufacturers have developed novel fast gas ***delivery*** hardware capability, but the complementary rapid gas ***evacuation*** capability remains largely overlooked. Chamber pumping strategies that can improve the efficiency of this rapid switching between very different flow volume regimes will be presented.

Apart from this extended pumping time requirement, these high-flow steps present other productivity challenges to the vacuum system. Historically, the chamber vacuum system was relied upon to deliver a low pressure using turbomolecular pumps (TMPs). These pumps operate spinning rotors at very high speeds to propel gases down and out of the pump. In general, the higher the gas flow rate, the more heat that is imparted to the TMP rotor and the higher the rotor temperature. However, a hot rotor poses two challenges: creep and corrosion, the rates of both are increased at higher temperatures. Rotor creep is deformation due to sustained stress and temperature and increases exponentially with temperature (See Figure 1). Furthermore, condensable etch by-products need to be managed by controlling the internal pump temperature profile to ensure that surfaces in the gas path are hot enough to keep the by-product in the vapour phase. In addition, the adoption of specific surface passivation and protection techniques, utilising precursor deposition chemistry, (e.g. in-situ ALD / ALE) intensifies this challenge of by-product management within the vacuum system.

This paper will not only discuss how internal pump technology can help address these challenges, but also how different chamber pumping strategies can be deployed to this end.

2:30pm **ALE1-TuA-5 Mechanistic Study of the Thermal Atomic Layer Etch of Cobalt Metal Using Propene and CO***, **Suresh Kondati Natarajan**, M Nolan,* Tyndall National Institute, Ireland*; P Theofanis, C Mokhtarzadeh, S Clendenning,* Intel Corp.

Due to the possibility of improved electromigration properties and lower resistivity at decreased critical dimensions, Co has been identified as a candidate to replace Cu and potentially W in future semiconductor devices. To enable the use of Co at such small dimensions, monolayer control in processing is desirable. Accordingly, Atomic Layer Etch (ALE) functions as a complementary process technique to well-established Atomic Layer Deposition (ALD) methodologies, such that sequential self-limiting etch

processes can be targeted with monolayer control for ultra-thin film material removal.

Herein, we present a theoretical analysis using first principles simulations of a thermal ALE process for cobalt metal utilizing a sequential thermal-chemical etch cycle employing propene and carbon monoxide (CO). It is shown that ALE can be achieved via the oxidative addition-H_2 elimination of propene to the Co surface followed by the introduction of CO to generate $(\eta^3\text{-}C_3H_5)Co(CO)_3$ as a volatile etch product at process conditions. It was found that the generation of $(\eta^3\text{-}C_3H_5)Co(CO)_3$ is thermodynamically favourable and necessitates a high CO step coverage. A full proposed mechanism for this potential thermal atomic layer etch process will be discussed.

2:45pm **ALE1-TuA-6 Selective Quasi-ALE of SiO_2 over Si_3N_4 via Bottom-up Si_3N_4 Passivation: A Computational Study***, **Du Zhang**, Y Tsai, Y Shi, M Wang,* TEL Technology Center, America, LLC

Selective SiO_2/Si_3N_4 atomic layer etching (ALE) has broad applications in both logic and memory device fabrication. Conventional methods of achieving SiO_2/Si_3N_4 selectivity generally employ a preferential top-down carbon-based polymer passivation on Si_3N_4. However, achieving a highly preferential passivation of Si_3N_4 only is challenging in this top-down carbon polymerization approach. To overcome these limitations, we propose a two-step selective $SiO_2/Si_3N\text{-}_4$ ALE method that utilizes bottom-up $Si_3N\text{-}_4$ passivation. In the first step, the formation of an ammonium (NH_4^+) salt blocking layer on the Si_3N_4 surface is enabled in a plasma containing H_2 and HF via surface conversion, with its feasibility and reaction pathways demonstrated with thermodynamics and quantum chemistry calculations. The SiO_2 substrate, by contrast, undergoes a partial surface reduction by the H radicals, demonstrated with molecular dynamics simulations. In the second step, the partially reduced SiO_2 surface can be volatilized in a plasma containing fluorine and/or other halogens, leaving the Si_3N_4 underneath the NH_4^+ salt layer intact. This new approach provides a promising solution toward infinite SiO_2/Si_3N_4 selectivity, thanks to the N atoms for the NH_4^+ salt passivation layer provided by the Si_3N_4 substrate alone. Moreover, the bottom-up passivation also translates into better pattern fidelity due to precise etch control, which is essential for the ever-shrinking CD of devices.

3:00pm **ALE1-TuA-7 Insights of Different Etching Properties between CW and ALE Processes using 3D Voxel-Slab Model***, **Nobuyuki Kuboi**, T Tatsumi, J Komachi, S Yamakawa,* Sony Semiconductor Solutions Corp., Japan **INVITED**

Atomic layer etching (ALE) processes have attracted considerable attention to realize high control etching (layer-by-layer) and very low damage (defect creation) caused by ion bombardment from plasma [1]. To use ALE as a practical process in mass production of semiconductor devices, it is necessary to know how to control process nobs along with the mechanism. To obtain such knowledge in the view point of numerical simulations, we modeled the ALE process of SiO_2 and Si_3N_4 films and simulated etching properties in the cases of conventional continuous-wave (CW) etching and ALE.

We propose a surface reaction model for the ALE process which consists of a deposition step by $C_4F_8/O_2/Ar$ plasma and etch step by Ar plasma for SiO_2 and Si_3N_4 film etching. This is based on the slab models of SiO_2 [2] and Si_3N_4 [3], which can give not only the etch rate and thickness of the C-F polymer layer but also the damage distribution described by Si dangling bond density on the etched layers. he surface layer is assumed to consist of two layers: a reactive layer divided by several thin slabs of lattice size order and a deposited C-F polymer layer on the reactive layer. We considered not only outflux of O and N from the reactive layer described previously [2][3] but also the enhancement effects of F from the deposition step and the etched polymer layer by an Ar^+ ion on the etch yields of SiO_2 and Si_3N_4 films by the Ar^+ ion. To analyze the 3D etched profile for the self-aligned contact (SAC) process, we developed a 3D simulation technique using an advanced voxel model (called "smart voxel"), which also includes the slab model with the above surface reactions.

From the simulations for blanket film wafer and SAC etching compared with CW and ALE processes using our 3D voxel-slab model, we found that the use of monochromatic ion energy improve the controllability of surface layer thickness (polymer layer and reactive layer) and that quantitative control of the time variation of both the polymer layer thickness and ion penetration depth are necessary for low damage. Furthermore, relatively high SiO_2 etch rate (~ 40 nm/min) with high selectivity (> 100) can be obtained after optimizing polymer layer thickness, ion energy, and cycle time. For realizing higher performance of ALE, accurate prediction of the surface reaction and further quantitative control of the plasma parameters are necessary.

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Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE2-TuA
Modeling & Instrumentation II

Moderators: Dmitry Suyatin, Lund University, Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation

4:00pm **ALE2-TuA-11 First-principles Understanding of Atomic Layer Etching of Silicon Nitride using Hydrofluorocarbons***, **Gyeong Hwang**, E Cheng,* University of Texas at Austin*; S Sridhar,* TEL Technology Center, America*; P Ventzek, A Ranjan,* Tokyo Electron America Inc.

The removal of thin layers of material with atomic-scale precision and spatial control (area selectivity) is critical for advanced device fabrication, making atomic layer etching (ALE) more attractive due to its ability to tightly control etch rates and to achieve wafer scale uniformity without physical damage. While ALE processes have been widely used to remove Si, Ge, compound semiconductors, and various oxides, only a few studies on ALE of Si_3N_4 films have been reported despite its technological importance. Recent experimental investigations have demonstrated that ALE of Si_3N_4 can be achieved via sequential exposure of hydrogen and fluorinated plasma or a cyclic process involving two alternating CH_3F gas adsorption and Ar^+ bombardment steps. Both methods are avenues for area selective etch and isotropy control. However, the fundamental mechanisms by which the etching occurs are poorly understood. In this talk, we will present our recent findings regarding underlying mechanisms leading to facile ALE of Si_3N_4 using hydrofluorocarbons, based on periodic density functional theory calculations. Our study highlights the important role of adsorbates and surface functional groups. For CH_3F chemisorption on a N-rich Si_3N_4 surface, we have found a trimolecular process to be the thermodynamically most favorable pathway for initiation of the process, consisting of a nucleophilic attack of a primary amine site, if available, on CH_3F, followed by a stabilization of the fluoride leaving group by an adjacent primary amine site. While this mechanism as is has a relatively high activation energy (~0.9 eV), the presence of products from other reactions on the surface such as HF, F^-, and H^+ have been demonstrated to lower this activation energy significantly. Furthermore, we find that it is not the methylation of the surface that facilitates etching, but rather the production of H^+/F^- that helps facilitate formation of volatile N-containing species and Si-F bonds. More importantly, our study also suggests that the surface reaction mechanism responsible for Si_3N_4 ALE may be altered when CH_3F is replaced by CHF_3 or CF_4.

4:15pm **ALE2-TuA-12 An Extended Knudsen Diffusion Model for Aspect Ratio Dependent Atomic Layer Etching***, **Luiz Felipe Aguinsky**, P Manstetten,* TU Wien, Austria*; A Hössinger,* Silvaco Europe Ltd., UK*; S Selberherr, J Weinbub,* TU Wien, Austria

Atomic layer etching (ALE) is a fundamental part of semiconductor processing as device critical dimensions must be controlled to the order of nanometers [1]. One known issue in ALE, as in other etching processes, is aspect ratio dependent etching (ARDE) [2], which is the reduction of etch rates as the aspect ratio of a feature increases. One of the mechanisms linked to ARDE is the depletion of neutral species towards the bottom of a feature. This phenomenon has been investigated using a three-dimensional Monte Carlo method [3]. However, this method requires a complex setup and it is computationally expensive. For deposition processes, Knudsen diffusion [4] models provide analytical results and are actively developed. These models have been used for estimating surface parameters in some atomic layer deposition processes [5]. The Knudsen diffusion approach arises from physical considerations to the mass balance at each volume element. Alternatively, given isotropic reflections and particle source, the fluxes can be calculated exactly over the whole domain via the radiosity equation [6]. The radiosity approach requires the assembly and inversion of a matrix describing the exchanges, being notably unsuitable for low sticking regimes.

We propose a model extending the standard deposition Knudsen diffusion approach by including the direct flux from a particle source and a geometric factor to enable a more rigorous picture of ARDE in ALE. The inclusion of the direct flux is motivated by the radiosity equation, while avoiding the costly matrix inversion step. The geometric factor enables a more accurate description of the geometry by integrating over the whole feature at each volume element. We compare our extended Knudsen diffusion model against a reference radiosity model [6], achieving good agreement. Our results highlight one shortcoming of the standard Knudsen diffusion model: The flux near the bottom of a high aspect ratio feature is underestimated. We also show that the geometric factor describes the particle transport more accurately near the extremities of finite cylinders.

The financial support by the Austrian Federal Ministry for Digital and Economic Affairs and the National Foundation for Research, Technology and Development is gratefully acknowledged.

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4:30pm **ALE2-TuA-13 Thermodynamics-Based Screening Approach for Atomic Layer Etching*, Nagraj Kulkarni,*** Unaffiliated

A thermodynamics-based approach for screening directional or thermal Atomic Layer Etching (ALE) processes is discussed for the purpose of achieving high synergies close to unity. The Ta-Cl system was selected as a test case for this analysis. Reaction equilibria for over 30 condensed-gas species were computed from available thermodynamic data in this system. Suitable process conditions for the formation of stable reaction products or compounds and the corresponding partial pressures of known gas species were first obtained with the aid of volatility diagrams that were calculated using thermodynamic data for all known solid-gas reactions. For optimum conditions during the first stage of a typical ALE process (passivation step), the selection of suitable metal-gas compound/s that have very low vapor pressures and hence negligibly low etch rates was made. For optimum conditions during the second stage (inert ion sputtering) of a directional ALE process, an assessment of the potential for selective sputtering of the selected compound/s relative to the base metal was made from knowledge of the surface binding energies of the base metal and relevant compound/s that are usually considered to be the enthalpy changes of the relevant solid-gas sputtering reactions at room temperature. In the case of an isotropic, thermal ALE process, the selection of suitable temperatures for the direct volatilization of the reaction product layer during the second stage of ALE is also discussed.

4:45pm **ALE2-TuA-14 Always in Competition: Self-limiting Versus Continuous Reactions in ALD and ALEt*, Simon D. Elliott,*** Schrödinger, Inc.*; S Natarajan, R Mullins, M Nolan,* Tyndall National Institute, Ireland*; A Cano, J Clancey, S George,* University of Colorado - Boulder

One of the main challenges in designing novel atomic layer deposition (ALD) and atomic layer etch (ALEt) processes is to ensure the self-limiting (SL) nature of reactions during the individual precursor pulses at the target temperature of interest. It is important to establish a SL temperature window to ensure that the precursors will not produce chemical vapour deposition (CVD) or chemical vapour etching (CVE). To that end, we have developed a first principles based computational methodology to study the competition between continuous and SL reactions when a material surface is exposed to precursor gases.

ALEt processes for oxides have been reported using sequential fluorination by HF and ligand exchange reactions at elevated temperatures.[1] Herein, we investigate the nature of the HF pulse when treating a range of materials including B_2O_3, TiO_2, HfO_2, ZrO_2, Al_2O_3 and TiN by comparing the free energy profiles of the potential CVE and SL reactions computed with density functional theory (DFT). In general, elevated temperatures favour CVE of these materials, whereas fluorination of the surface is self-limiting at lower temperatures. HF was computed to continuously etch B_2O_3 and TiO_2 even at temperatures below 100°C by forming volatile fluorides. This is in good agreement with experimental FTIR, where the onset of continuous etching of TiO_2 by HF was found at 80°C – 90°C and where etching of B_2O_3 proceeded even more rapidly than that of TiO_2. However, in another example, HF is predicted to preferably etch HfO_2 above 160°C, whereas experiment[1] shows the process to be still self-limiting at 200°C. Therefore, this simple thermodynamic analysis, which does not include reaction kinetics, is only able to provide a lower threshold temperature at which a CVE reaction may become favourable, subject to overcoming any kinetic barrier. We also computed that Al_2O_3 resists continuous etching up to 340°C while TiN can not be etched until temperatures exceed 1300°C.

This methodology is also used to understand the competing CVD and SL reactions in the ALD of Ru using the RuO_4 precursor and H_2.[2] The DFT calculations show that RuO_4 undergoes an SL decomposition into RuO_2 on electron-rich surfaces and that this is in competition with CVD.

These examples illustrate that this relatively quick computational approach can be effectively used to screen candidate precursor molecules to be selected for material processing.

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5:00pm **ALE2-TuA-15 Variation of Etched Depth per Cycle and Removal of Reactive Species in Atomic-Layer Etching (ALE) : Molecular Dynamics Study*, Satoshi Hamaguchi,*** *E Tinacba, S Shigeno, Y Okada, M Isobe, T Ito, K Karahashi,* Osaka University, Japan

Alternating application of reactive species from a plasma with no bias energy and Ar plasma with low bias energy to a Si-based film (such as Si, SiO2, and SiN) can cause atomic layer etching (ALE) of its surface. In this process, the initial application of reactive species to the surface will leave a sufficient number of reactive species (e.g., Cl atoms) bonded with the surface atoms (e.g., Si, forming Si-Cl bonds) and, in the second step where low-energy Ar+ ions irradiate the surface, a thin mixed layer of the reactive species and surface atoms is formed and volatile molecules (e.g., SiCl4) desorb from the surface. Since the incident energy of Ar+ is too low to physically sputter surface atoms, etching or desorption of volatile species ends as soon as reactive species are exhausted from the surface - even if Ar+ ions continue to bombard the surface with low incident energy. This self-limited etched depth of a single cycle (i.e., application of reactive species and application of low-energy ions) allows “nearly” layer-by-layer etching of the material surface. At the end of each cycle, where self-limited etching takes place, some reactive species tend to remain on the surface or in the subsurface region, causing surface roughness. Depending on how deep such reactive species diffuse into the subsurface region or how thick the formed mixed layer becomes, the etched depth per cycle changes. In this study, etched depth per cycle and remaining reactive species are discussed based on the results of molecular dynamics (MD) simulation of single cycles of various ALE processes. Example considered here include Si ALE by fluorine reactions, SiO2 ALE by fluorocarbon reactions,

And SiN etching by hydrofluorocarbon or hydrogen reactions.

Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE1-WeM
Integration & Application of ALE

Moderators: Bert Ellingboe, Dublin City University, Wei Tian, Applied Materials Inc.

8:00am **ALE1-WeM-1 ALD and Etch Synergy to Enable the Next Scaling Innovations***, **Angelique Raley**, K Lee, X Sun, Q Lou, Y Lu, M Edley, S Oyola-Reynoso, P Ventzek, R Clark, P Biolsi, H Masanobu, A Ranjan,* TEL Technology Center, America, LLC **INVITED**

As logic nodes continue to scale below 7 nm, the back-end-of-line (BEOL) critical pitch has moved to sub-40 nm and is forecasted to scale down to 14 nm according to the latest International Roadmap for Devices and System (IRDS). In addition to the patterning and integration complexities that arise with scaling, pitch reduction has a direct impact on the plasma-processing window. Conventional continuous wave processes can no longer achieve stringent aspect ratio dependent etching (ARDE), selectivity and profile control requirements and have gradually given way to pulsed plasma processes, decoupled process sequence plasmas or remote plasmas to widen the process space. In this talk, we will discuss implementation of atomic layer deposition (ALD) and decoupled or cyclic plasma etch in the BEOL to overcome challenges of mask loss, ARDE, low k damage and LER/LWR and look to future technology enablement with area and topographically selective processes.

ALD processes are achieved by using sequential, self-limiting reactions. ALD technology is widely used to go beyond lithography resolution limits, to increase selectivity and to enable self-alignment. For dielectric etches with fluorocarbon plasma chemistry a decoupled plasma etch process can achieve the benefits of an ARDE free etch with improved mask selectivity.

Integrations combining ALD and etch can yield further improvements in profile such as chamfer control and via CD control which have a direct impact on device reliability and yield. Finally, cyclic combinations of ALD and etch can drive down line width roughness through smoothing benefits of front growth merging and preferential etching of asperities.

8:30am **ALE1-WeM-3 On the Role of Individual Etching Components in Selective Atomic Layer Processing: Etch and Deposit to Obtain High Selectivity***, **Alfredo Mameli**,* TNO/Holst Center, Netherlands*; F Roozeboom,* Eindhoven University of Technology and TNO, Netherlands*; P Poodt,* TNO/Holst Center, Netherlands **INVITED**

In the domain of Atomic Layer Processing both Atomic Layer Etching (ALE) and area-selective Atomic Layer Deposition (ALD) are becoming increasingly popular because of their potential in advancing nanomanufacturing.[1, 2] Yet, the selectivity in terms of layer thickness and defectivity requirements has major limitations to overcome. Here, the combination of selective deposition and etching can play a key role in tackling these challenges.[3, 4] The complementarity of deposition and etching techniques offers great potential for reaching the targeted requirements for advanced applications.

In this presentation, the combination of spatial area-selective ALD using chemoselective inhibitors and interleaved etching steps to increase the process selectivity will be discussed. The focus will be on two different etching steps: the self-limiting etching of the inhibitor and a blanket etch-back step of the growing material. The former enables cyclic selective deposition when using a plasma-based ALD process while the latter allows for further maximizing the selectivity.

Finally, the concept of area-selective ALD combined with etching techniques in an integrated cyclic etch/dep spatial-tool for high-throughput Atomic Layer Processing will be presented.

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9:00am **ALE1-WeM-5 Area-Selective Deposition of TiO_2 on Various Surfaces by Isothermal Integration of Thermal TiO_2 ALD and ALE***, **Seung Keun Song**, G Parsons,* North Carolina State University

As transistor size is shrinking, area selective deposition process is becoming more important than before. Atomic Layer Deposition (ALD) and Atomic Layer Etching (ALE) are promising processes for area selective deposition of metallic and dielectric materials as they can deposit and etch nanoscale thickness of thin film conformally. ALD precursors usually have different affinity to solid surfaces, which enables ALD processes to have surface dependent selectivity. For examples, thermal TiO_2 ALD, employing sequential doses of $TiCl_4$ and H_2O, shows initial growth delay on hydrogen-terminated silicon (Si-H) but rapid growth on oxide silicon surface (SiO_2) at 150-190°C. To extend this surface dependent selectivity, we created isothermal integrated ALD/ALE process, where TiO_2 ALD cycles are combined with a few cycles of thermal TiO_2 ALE, employing sequential doses of WF_6 and BCl_3, under isothermal condition. Using the integrated ALD/ALE sequence, we achieve ~ 7 nm of TiO_2 on SiO_2, before noticeable TiO_2 nucleation on Si-H, as determined by SEM, ellipsometry and TEM analysis. Process and materials analysis using in-situ QCM and ex-situ AFM and XPS further confirm our findings. Beyond TiO_2 selectivity on Si/SiO_2 surfaces, some metal surfaces (Cu, Au, Co) showed some extent of initial growth delay during TiO_2 ALD cycles, as observed by in-situ QCM. Thus, TiO_2 selectivity on various kinds of surfaces was also studied with ex-situ XPS, SEM, and ellipsometry. We expect that this demonstrated ALD/ALE process on various surfaces provides useful information about ALD/ALE precursors reactions on various surfaces, and this information offers opportunities to integrate ALD and ALE process with optimum process controls.

9:15am **ALE1-WeM-6 Limited Dose ALE and ALD Processes for Local Film Coatings on 3D Structures***, **Thomas Seidel**,* Seitek50*; M Current,* Current Scientific

The use of limited dose ALE and ALD are described for producing localized film coatings on 3D, non-planar structures such as trenches and fins. Limited dose ALD (LD-ALD) has been described for improved ALD film deposition rate (thickness/unit time)[1] and for local masking applications of DRAM bottle trenches.[2] In this paper we describe Limited Dose Atomic Layer Etch (LD-ALE) to obtain localized films on trenches and fins using various combinations of standard ALD, LD-ALD and LD-ALE. Three cases for localized film coatings are described:

(I) a film localized at the bottom of a trench or fin, by using standard ALD followed by LD-ALE,

(II) a film localized at the center of a trench or fin, using LD-ALD followed by LD-ALE, and

(III) a film localized at the top and bottom of a trench or fin, using ALD followed by LD-ALE, and this in turn followed by LD-ALD.

In case (I), the LD-ALE step is carried out using a prescribed limited ALE precursor modification[3] dose. The limited dose is prescribed to attain the desired local film etching and removal of a specified depth near the top of the non-local feature. As an application example, the local doping at the bottom of a bulk finFETs, is described using doped ALD films[4] at the bottom of a fin to counter dope the base of the fin. Separately, doping the source – drain region at the top of the fin is described. Examples of mask applications on trenches and fins will be described, as well as film localized thickness adjustments. Limited Dose implementation challenges as well as various equipment opportunities are briefly discussed. If experimental demonstrations are available, they will be presented.

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9:30am **ALE1-WeM-7 Formation of Ohmic Contacts to Si using In-situ Chemical Cleaning of the Substrate***, **Sara Iacopetti**,* Technion - Israel Institute of Technology, Israel*; R Tarafdar, S Lai, M Danek,* Lam Research Corp.*; M Eizenberg,* Technion - Israel Institute of Technology, Israel

The implementation of novel device geometries in CMOS technology such as FinFETs, allowed a further downscaling of the logic nodes to 45 nm and below, reaching nowadays mass production of devices of 7 nm and studies on sub-5 nm nodes. To such feature sizes and complex geometries, the well-established technology of Source and Drain (SD) contacts by metal silicide formation produces bulky contacts that cause short-channel effects,

detrimental to the transistor performances. Shallow ohmic contacts must be implemented in the future.

This work focuses on the feasibility of producing ohmic contacts using in-situ chemical cleaning (CC) of the native SiO_2 layer prior to the deposition of the contact metal (Co) without air break. The two main aspects investigated are the amount of Si consumption as a function of heat treatment, and the resultant contact resistivity.

Si blanket wafers were exposed to different number of cleaning cycles (increasing: No CC, CC-, CC+ and CC++); Co was deposited by PVD to isolate the effect of cleaning on the interface. Compositional and microstructural studies were carried by ToF-SIMS, XRD and HRTEM (STEM-EDS) on Si + 30 nm PVD Co, as-deposited and vacuum annealed. The CC removes completely the native oxide but creates a disordered interlayer of 2 nm thickness at the metal/semiconductor interface. Cobalt silicides formation is accelerated as a consequence of the removal of the native oxide, leading to the formation of a Co and Si intermixed layer from 200°C, and the onset of crystalline CoSi and $CoSi_2$ formation as early as 350°C and 450°C, respectively. As the resulting contacts are very thick (> 60 nm for the low thermal budget annealing), the approach to shallow contact fabrication moved to Si(CC) + PVD Co 10nm/TiN 30 nm/Co 200nm, without air break between depositions. The thin silicide formation with annealing of the contacts was checked by TEM and XRD and it follows the same silicide formation as seen in the Si + PVD Co 30nm case.

The contact resistivity was studied by fabrication of structures for transmission line measurement (TLM) by photolithography on Si/Co/TiN/Co, followed by wet or reactive ion etching of the metals. The contacts are ohmic and specific contact resistivities of 10^{-6} Ωcm^2 were measured, higher for the CC++ samples with respect to the non-cleaned and other cleaned samples, suggesting that the disordered interface plays a role as a thin dielectric barrier across the interface.

The ongoing research is focusing on the quantitative study of the interface composition and its influence on the contact resistivity, crucial for moving to an ALD metallization scheme.

9:45am **ALE1-WeM-8 SADP Spacer Profile Engineering by Quasi-Atomic Layer Etching***, **Tsai Wen (Maggie) Sung**, C Yan, H Chung, J Lo, D Desai, P Lembesis, R Pakulski, M Yang,* Mattson Technology, Inc.

As the size of modern device shrinks, self-aligned double patterning (SADP) and quadruple patterning (SAQP) has gained increasing interest in the fabrication of 14nm technology node and beyond. Plasma reactive ion etching (RIE) with inductively coupled plasma (ICP) is a common technique utilized in the SADP/SAQP process flow because of its etch anisotropy and tunability. Higher bias power is usually employed to achieve sufficient directionality; however, it can lead to sloped, sharp, and asymmetric spacer profiles. These undesired profiles may cause inadequate pattern transfer and the error may be amplified as it moves down the process line, such as pitch-walking and nonuniform fin formation. Furthermore, a high bias power can also severely damage the bottom substrate due to strong ion bombardment, resulting in an uneven etch. Recently, a method for quasi-atomic layer etching (QALE) was developed where it was found that the reactivity of a material increased with exposure to an active species.[1]

In this work, a chemical dry etch (CDE) equipment with an ICP radical source and a capacitively coupled plasma (CCP) plasma source was utilized to perform QALE. A RF bias was applied to the substrate to produce highly selective radicals and to promote vertical implantation of the active species into the top surface of SADP spacers. The implantation "activates" the spacer top surface by increasing its etch rate during a subsequent etch step, while keeping the etch rate of the unexposed sidewalls at a minimum, thereby improving the etch anisotropy. The activation-etch process is self-limiting and the etch depth scales linearly with the activation-etch cycles. By modulating this QALE method, we successfully demonstrated a significant reduction of the spacer shoulder slope and tip angle, thus flattened the spacer profile. Moreover, the QALE technique can be further developed and utilized to engineer the spacer surface profile and applied in other device fabrication processes.

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Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE2-WeM
Materials Selective ALE

Moderators: Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, Geun Young Yeom, Sungkyunkwan University

10:45am **ALE2-WeM-12 Dynamic Temperature Control Enabled Atomic Layer Etching of Titanium Nitride***, **He Zhang**, Y Kim, D Paeng,* Lam Research Corp.

TiN ALE was achieved with Rapid Thermal Sources using O_2 plasma and Cl_2. TiN surface was oxidized to TiO_2 and the following Cl_2 flow absorbed Cl on the oxidized surface. This modified layer can be thermally removed under intense light source irradiation. Full removal of few nm blank ALD TiN layer is demonstrated. XPS observed surface composition change after each step. Surface smoothen was also observed after etching. The ultra-short thermal pulses enabled fine control of surface reactions in each ALE steps. Thermal ALE of Ge under similar approach will also be discussed.

11:00am **ALE2-WeM-13 Rapid Thermal-Cyclic Atomic Layer Etching of Thin Films with Highly Selective, Self-Limiting, and Conformal Characteristics***, **Kazunori Shinoda**,* Hitachi, Japan*; H Kobayashi,* Hitachi*; N Miyoshi, M Izawa,* Hitachi High-Technologies*; K Ishikawa, M Hori,* Nagoya University, Japan **INVITED**

Etching processes with atomic level precision are important in order to provide next-generation of semiconductor devices that have densely arrayed high-aspect-ratio structures. There is thus considerable interest in the development of isotropic atomic layer etching (ALE) for a variety of materials used in semiconductor manufacturing. One approach for isotropic ALE is rapid thermal-cyclic ALE, which consists of cyclic repetitions of plasma exposure at lower temperature and infrared (IR) lamp annealing. The plasma exposure produces self-limiting modified layers on the surface of the target materials, and the IR lamp annealing removes the modified layer by thermal desorption. The authors demonstrated rapid thermal-cyclic ALE of a variety of materials such as Si_3N_4, SiO_2, TiN, and W over the last several years.

Rapid thermal-cyclic ALE processes were originally developed on the basis of an understanding of plasma-surface reactions using in-situ analysis. As for Si_3N_4, in-situ x-ray photoelectron spectroscopy (XPS) analysis revealed that hydrogen and fluorine containing plasmas produce a self-limiting layer of ammonium hexafluorosilicate on the surface of Si_3N_4. Thermal desorption spectroscopy (TDS) analysis showed that lamp annealing decomposes the ammonium hexafluosilicate into SiF_4, HF, and NH_3. The result of TDS is consistent with the result of thermodynamic calculation of the decomposition of ammonium hexafluorosilicate. This technology is also applicable to other nitride films besides Si_3N_4. The authors have demonstrated self-limiting isotropic ALE of TiN using this technology.

A 300-mm ALE apparatus that consists of an inductively coupled plasma (ICP) source for downflow radicals, IR lamps for rapid thermal annealing, and in-situ ellipsometry for thickness monitoring was developed for rapid thermal-cyclic ALE. A self-limiting nature in both the plasma exposure step and the lamp annealing step has previously been demonstrated for Si_3N_4, TiN, and W. Conformal, highly selective etching for patterned samples was confirmed by transmission electron microscopy (TEM). Layer by layer ALE for Si_3N_4 of more than 100 cycles was confirmed by in-situ ellipsometry. Moreover, it was demonstrated that etching selectivity between different materials could be switched from infinitely selective to nonselective by adjusting the lamp annealing time. In this talk, applications of rapid thermal-cyclic ALE for a variety of dielectric and metal films will be presented.

11:30am **ALE2-WeM-15 Atomic Layer Etching of HfO_2 with Selectivity to Si by Utilizing Material-Selective Deposition Phenomena***, **Kang-Yi Lin**, C Li,* University of Maryland*; S Engelmann, R Bruce, E Joseph,* IBM T.J. Watson Research Center*; D Metzler,* IBM Research - Albany*; G Oehrlein,* University of Maryland

Atomic layer etching (ALE) applies sequential deposition, reactant purge and etching steps with a short processing step length to establish self-limited material removal and atomic scale precision. The reactants during the ALE deposition steps may exhibit material-selective deposition based on the chemical affinity of precursor gases to the substrate material and nature of interfacial bonding. Integrating the feature of material -selective deposition with an etching step opens a new processing window for selective ALE. In this work, we evaluated the deposition behaviors of

different hydrofluorocarbon (HFC) precursors, i.e. mixtures of methane (CH_4) with trifluoromethane (CHF_3) and mixtures of methane with octafluorocyclobutane (C_4F_8), on Si and HfO_2 surfaces, respectively. This is followed by the investigation of substrate-dependent selective deposition using a mixture of HFC precursors to achieve HfO_2 etching and etching selectivity relative to Si. Our results show that during the purge step of ALE sequences using CH_4/CHF_3 selectively deposit a fraction of a nm thick FC layers on Si surface while self-desorption is observed on the HfO_2 surface . In contrast, mixtures of CH_4 with C_4F_8 etchant do not show this self-desorption behavior for HfO_2. By utilizing the selective deposition behavior seen for CH_4/CHF_3-based ALE in conjunction with low energy Ar ion bombardment, we were able to remove the top HfO_2 layer while simultaneously forming a FC passivation layer on the underlying Si surface. In order to confirm the etching performance of CH_4/CHF_3-based ALE of HfO_2, X-ray photoelectron spectroscopy (XPS) was used to study whether any HfO_2 remains on the sample at the end of the processing cycle where the in-situ ellipsometry indicated a depletion of the HfO_2 layer . The XPS results show that after the ALE processing the Hf-O peaks no longer exist in the Hf4f and O1s spectra. Instead, a weak intensity of the fluorinated Hf peaks are observed, suggesting the HfO_2 layer with an initial thickness of 2.9 nm was removed and a few hafnium etching byproducts were left on the substrate. These results support the concept that gas pulsing of complex HFC precursors during ALE sequences provides the opportunity to achieve material-selective deposition and enable ALE selectivity of HfO_2 relative to Si.

11:45am **ALE2-WeM-16 Enhancing Etch Selectivity in Plasma-Assisted ALE of Silicon-Based Dielectrics using Surface Functionalization***, **Ryan Gasvoda,*** Colorado School of Mines*; S Wang, E Hudson,* Lam Research Corp.*; S Agarwal,* Colorado School of Mines

Stringent processing windows are required for the fabrication of sub–7–nm semiconductor devices, which in turn places severe constraints on conventional plasma-–assisted etching. Atomic layer etching (ALE) is a promising etching technique that can provide high etch fidelity, directionality, layer–by–layer removal, and selectivity to meet the stringent processing demands. Plasma–assisted ALE of SiO_2 and SiN_x typically consists of two sequential half–cycles: fluorocarbon (CF_x) deposition from a fluorocarbon plasma followed by an Ar plasma activation step. Typically, selectivity is achieved through manipulating the plasma and processing parameters. Recently, we proposed a methodology to further increase etch selectivity by selective prefunctionalization of the SiO_2 or SiN_x surface with hydrocarbons. We show that the abundance of hydrocarbon on the prefunctionalized surface promotes the formation of an etch inhibiting graphitic carbon film after just a few ALE cycles.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and *in situ* 4–wavelength ellipsometry during ALE to monitor the surface reactions, film composition, and net film thickness. We show that cyclic azasilanes can be used to selectively functionalize SiO_2 over SiN_x. Figure 1 shows the infrared spectra after 5 ALE cycles of SiO_2 etching with (blue) and without (black) surface prefunctionalization. For the prefunctionalized surface, we observe an increase in absorbance from ~1500 – 1800 cm^{-1}, assigned to a graphitic hydrofluorocarbon film. After just 4 ALE cycles, this graphitic hydrofluorocarbon film reaches a thickness that acts as an etch stop layer. As a result, after 10 cycles, the etched thickness of SiO_2 was ~23% of the case where there was no surface functionalization. This methodology can therefore be used to enhance overall etch selectivity for SiN_x over SiO_2. Further, we will discuss the role of Ar^+ ion energy during the Ar plasma activation step on graphitic hydrofluorocarbon film formation. The length and structure of the hydrocarbon chain on the prefunctionalized surface will also be addressed.

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