

Atomic Layer Etching

Room 104-106 - Session ALE1-MoA

Plasma and/or Energy-enhanced ALE I

Moderators: Bert Ellingboe, Dublin City University, Satoshi Hamaguchi, Osaka University, Japan

1:30pm ALE1-MoA-1 Investigation of Atomic Layer Etching Process and UV Damage for AlGaIn/GaN HEMT, Hiroyuki Fukumizu, Toshiba Memory Corporation, Japan; *K Kanomaru,* Toshiba Corporation, Japan; *T Kikuchi,* Toshiba Corporation

INVITED

Gate-recess type of AlGaIn/GaN for high electron mobility transistor (HEMT) is one of the devices which can operate normally-off for high power electronics applications. This gate-recess structure demands precise control of etching depth and minimization of etching damage to AlGaIn film. In previous atomic layer etching (ALE) studies for GaN or AlGaIn, it was first reported that the surface was oxidized by O₂ plasma and then subsequently this surface was removed by BCl₃ plasma [1]. Recently, a directional type of ALE for GaN and AlGaIn films using Cl₂ or BCl₃/Cl₂ plasma and Ar ion bombardment was investigated and the surface roughness of GaN film etched by ALE was more suppressed than RIE [2]. We investigated the etching process property and UV damage on AlGaIn film and compared them between ALE and conventional RIE.

AlGaIn films were etched by Cl₂/Ar chemistry for RIE. In case of ALE, a modified layer was formed by exposure to Cl₂ plasma and then, this modified layer was removed by Ar ion bombardment. The etched surface roughness was evaluated by AFM and the surface roughness etched by RIE increased with etching. On the contrary, the surface etched by ALE showed a relatively smooth surface regardless of the etched depth. The increase of surface roughness etched by RIE is supposed to be due to lack of nitrogen of AlGaIn film, which is confirmed with XPS. To evaluate plasma induced damage, the etched surfaces were analyzed by cathode luminescence (CL). CL intensity of near band edge (NBE) of AlGaIn decreased after RIE and ALE. The degradation of NBE intensity of AlGaIn etched by ALE was more serious than RIE. This indicated that ALE process introduced higher damages on AlGaIn film than RIE. CL intensity of NBE of GaN, which was located under AlGaIn film, also decreased after RIE and ALE. This degradation etched by ALE was larger than RIE. The residual thickness of AlGaIn film was thick enough to protect the penetration of ions into GaN film underneath the AlGaIn film. From this result, it was supposed that damage of GaN film was introduced not by ions but UV photon radiation and this UV induced damage on GaN film brought by ALE was larger than RIE. This is supposed that ALE process time was longer than RIE and UV radiation amount of ALE was also larger than RIE.

[1] S. D. Burnham, K. Boutros, P. Hashimoto, C. Butler, D. W. S. Wong, M. Hu and M. Micovic, *Phys. Status Solidi C* **7**, 2010 (2010).

[2] T. Ohba, W. Yang, S. Tan, K. J. Kanarik and K. Nojiri, *Jpn. J. Appl. Phys.* **56**, 06HB06, (2017).

2:00pm ALE1-MoA-3 Plasma-assisted Atomic Layer Etching of Si-based Dielectric Films Studied using *in situ* Surface Diagnostics, Sumit Agarwal, *R Gasvoda,* Colorado School of Mines; *S Wang,* Lam Research Corp.; *R Bhowmick,* Colorado School of Mines; *E Hudson,* Lam Research Corp.

INVITED

The shrinking device dimensions in integrated circuits combined with the introduction of 3-D device architectures has created a need for atomic layer etching (ALE) processes for a variety of materials including Si-based dielectrics such as SiN_x and SiO₂. Development of new ALE processes that can meet the demands for semiconductor manufacturing requires an atomistic-level understanding of the surface reaction processes. In our group, in collaboration with Lam Research Corporation, we have pioneered the use of *in situ* optical diagnostic techniques including highly surface sensitive attenuated total reflection Fourier transform infrared spectroscopy and multi-wavelength ellipsometry to study the surface processes that occur during ALE.

In this presentation, I will discuss the atomistic-level details of an SiO₂ and SiN_x ALE process consisting of CF_x deposition from a C₄F₈/Ar plasma, and an Ar plasma activation step in which the CF_x film is activated, and the underlying substrates are etched. Sequential cycles of ALE of SiO₂ show a drift in the etch per cycle (EPC) with increasing cycle number. We attribute the drift in EPC to excess CF_x that is liberated from the reactor walls in the Ar plasma step. This increase in the EPC occurs even though the infrared

spectra confirm that the CF_x deposition onto the SiO₂ film is reproducible from cycle to cycle. To minimize the drift in EPC, Ar plasma half-cycles of twice the length are employed, which allows for the removal of CF_x from the reactor walls during each cycle, thus creating more reproducible chamber wall conditions. To further control the EPC, and obtain selective etching of SiN_x over SiO₂, we have explored selective attachment of surface functional groups such as hydrocarbons of different chain lengths. We have demonstrated that attachment of hydrocarbons to the surface prior to the start of ALE retards the EPC.

2:30pm ALE1-MoA-5 Silicon Atomic Layer Etching by Two-step Plasma-enhanced Atomic Layer Deposition Consisting of Oxidation and (NH₄)₂SiF₆ Formation, E Song, Korea Institute of Materials Science, Republic of Korea; *Ji-Hye Kim,* ISAC Research Inc., Republic of Korea; *J Ahn,* Korea Maritime and Ocean University, Republic of Korea; *J Kwon,* Korea Institute of Materials Science, Republic of Korea

The process of precise silicon etching on the atomic scale was investigated by examining the formation of an (NH₄)₂SiF₆ thin film as an intermediate phase followed by the removal of this layer by sublimation. An amorphous (NH₄)₂SiF₆ thin film was formed on a Si substrate via a two-step plasma-enhanced atomic layer deposition (PEALD) process consisting of an oxidation step involving an O₂ plasma and a transformation step to deposit an (NH₄)₂SiF₆ thin film using an NH₃ / NF₃ plasma, where the deposited thin film was removed by a sublimation process. Because the thickness of the (NH₄)₂SiF₆ thin film could be linearly controlled by altering the number of PEALD cycles, the etching depth could be successfully controlled on the sub-nanometer scale.

2:45pm ALE1-MoA-6 Factors in Selectively Etching SiO₂ over Si₃N₄ Using C₄F₈/Ar Atomic Layer Etching, Chad Huard, M Kushner, University of Michigan

Atomic layer etching (ALE) using fluorocarbon gas passivation offers several benefits over conventional etching, including increased selectivity enabled by low ion energies and increased control over polymer buildup.[1,2] This polymer is important in obtaining selective etching using fluorocarbon gases. During continuous etching the passivating fluorocarbon radical fluxes are generated by the same plasma as the activating ions, creating a close coupling between polymerizing and etching fluxes. These conditions result in limited operating conditions which produce selective etching of SiO₂. ALE offers a method to decouple the passivation/polymerization phase from the activating ions, enabling a new avenue to control selectivity.

In this presentation results will be discussed from a new computational model of the etching of silicon nitride and silicon dioxide by C₄F₈ containing plasmas. This new model, developed within the Monte Carlo Feature Profile Model (MCFPM), takes into account the transport of ion energy and radical species through a finite thickness polymer capping layer, including mixing and etching processes at the interface between the polymer and the material being etched. Applications to ALE in the context of self-aligned-contacts will be discussed.

Results from this model indicate that infinite selectivity to SiO₂ (over Si₃N₄) may be achievable in a pulse-periodic steady state ALE. This selectivity is possible because SiO₂ consumes more polymer during etching than Si₃N₄. When reactions with polymer by SiO₂ consumes all of the polymer deposited in each passivation phase of ALE, but the polymer consumed by Si₃N₄ is less than the amount deposited, a thick layer of polymer will form on a cycle to cycle basis on Si₃N₄. This thickening will eventually prevent etching of Si₃N₄, while SiO₂ continues to etch. Before reaching this state, there is a transient period where the polymer on Si₃N₄ is not yet thick enough to prevent etching, limiting the ability of ALE to provide perfect selectivity. In this initial period, the selectivity depends on many factors, including the ALE pulse times and the ion energy during the etching phase. Since ALE is often used to manage very thin films, the physics of this transient period where a finite amount of material is etched from both SiO₂ and Si₃N₄ takes on heightened importance.

[1] D. Metzler et al., *J. Vac. Sci. Technol. A* **32**, 20603 (2014).

[2] T. Tsutsumi et al., *J. Vac. Sci. Technol. A* **35**, 01A103 (2017).

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

3:00pm ALE1-MoA-7 Bias System for Controlling Ion Energy Distributions, Dan Carter, V Brouk, H Nguyen, Advanced Energy Industries, Inc.

Radio frequency voltage is commonly applied for generating bias in ALE and other traditional plasma processes. As device scaling drives the need for atomic precision, techniques for improving ion energy control continue

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to evolve. While methods combining frequencies¹ or harmonics², with and without phase control³ and even dynamic frequency variation⁴ have shown promise, the very nature of sine wave excitation is conflicting for achieving narrow or freely controlled Ion Energy Distributions (IEDs)⁵. We investigate a new power system utilizing optimized asymmetric voltage waveforms combined with a novel control system specifically designed for controlling wafer surface potential. Using this bias voltage application we evaluate the ability to directly manipulate surface bias and resulting IED's for producing single or multiple peaks with narrow or broad energy spread. We assess a metrology approach that allows the measurement of ion energy, ion current and sheath capacitance in real time. Near mono-energetic control across a wide energy range is demonstrated. Capability down to 10's of eV is shown for plasmas in the 10 to 100 mT range making this method suitable for many energy-sensitive, atomic scale plasma processes.

1. S. Shannon et al.; J. Appl. Phys. 97, 103304 (2005)
2. P. Diomedede et al.; Plasma Sources Sci. Technol. 23 (2014)
3. Y. Zhang et al.; J. Appl. Phys. 117, 233302 (2015)
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3:15pm ALE1-MoA-8 Reactions of Hexafluoroacetylacetone (hfac) and Metal Surfaces under Low-energy Ion Irradiation, Tomoko Ito, K Karahashi, S Hamaguchi, Osaka University, Japan

In recent years, atomic layer etching (ALE) by the formation of volatile organic transition-metal compounds has been expected to establish low-damage and atomically controlled etching processes for metallic thin films. Hexafluoroacetylacetone (hfac: $\text{CH}_2\text{F}_2\text{COCH}_2\text{COCF}_3$) is one of the candidates of organic ligands that may be used for atomic layer etching of Ni and Cu. Nigg et. al. have reported that Ni organic compounds desorb from a pre-oxidized Ni surface by hfac exposure and a control of the substrate temperature [1]. For the development of a highly anisotropic etching process, it is important to understand and control surface reactions of metal with an organic compound layer under low-energy ion bombardment. Therefore, our objectives of this study are to understand surface reactions by hfac exposure to a metal surface and to clarify effects of ion-induced reactions on hfac adsorbed metal surfaces. In this study, we have developed an atomic layer process (ALP) surface analysis system which consists of two parts: a high-resolution XPS analysis chamber and an ALP reaction chamber. After reactive gas exposure to a sample in the ALP reaction chamber, the sample can be transferred to the XPS chamber without air exposure of the sample. The hfac exposure was in the range of 100 - 10000L (in the units of L: Langmuir: 10^{-6} Torr · s) and Ni and Cu substrates are used in this study. The substrate temperature was set at room temperature. The hfac adsorbed surfaces were irradiated by low-energy Ar^+ ions (15- 50eV) and the changes in the chemical states were observed by XPS. It is found that, for pre-oxidized Ni and Cu surfaces, hfac molecules adsorbed without C-O and C-F bond breaking. It is also found that hfac adsorbed Ni-O surfaces are fluorinated by low-energy Ar^+ ion bombardment.

[1] H. L. Nigg and R. I. Masel, J. Vac. Sci. Technol. A, 17, 3477 (1999).

Atomic Layer Etching

Room 104-106 - Session ALE2-MoA

Plasma and/or Energy-enhanced ALE I

Moderators: Tetsuya Tatsumi, Sony Semiconductor Solutions Corp., Eric Joseph, IBM T.J. Watson Research Center

4:00pm ALE2-MoA-11 Application of ALE Technology to <10nm Generation Logic Device Fabrication, Jongchul Park, Samsung INVITED

As the design rule decreased gradually the dry etching technology has confronted with the severe limitations of etch loading and mask etch selectivity. Since the single RF powered CCP (Capacitively Coupled Plasma) was developed high frequency dual CCP, ICP (Inductively Coupled Plasma), DCS (DC Superposition) and RF pulsing have developed continuously to overcome those limitations. ALE technology was introduced recently as next generation etching technology to obtain very high performance at SAC (Self Aligned Contact) module of the high density logic device. But as the ALE consists of repeated deposition and etching the process controllability is very worse than the previous etching. We analyzed the control knobs for contact not-open and SAC shoulder fail to obtain much better performance for the mass production, and suggest the superior advantages of ALE over the conventional etching on the point of the fundamental limitations of the

dry etching and also recommend very essential technologies for better process capability of ALE technology.

4:30pm ALE2-MoA-13 Isotropic Atomic Layer Etching of ZnO on 3D Nanostructures, using Acetylacetone and O₂ Plasma, A Mameli, M Verheijen, A Mackus, W Kessels, Eindhoven University of Technology, Netherlands; Fred Roozeboom, Eindhoven University of Technology and TNO, Netherlands

The continuous driving force from the semiconductor industry for realizing smaller features and device structures with higher density and higher-aspect ratio poses increasing challenges in traditional etching techniques. Atomic layer etching (ALE) provides the opportunity to overcome the shortcomings of more conventional etching processes. Extensive research in this field has led to the development of two main classes: plasma ALE to achieve anisotropic etching and thermal ALE for the isotropic counterpart. Besides anisotropic etching, plasma can also be applied for achieving isotropic etch profiles. Yet, this process option has not been explored extensively.

In this work, we demonstrate isotropic ALE of ZnO on a regular array of vertical nanowires, using the alternated doses of O₂ plasma and acetylacetone (Hacac). A linear ZnO thickness decrease with increasing number of cycles was measured by *in-situ* spectroscopic ellipsometry, and saturation behavior was demonstrated for both Hacac and O₂ plasma, at 250°C. The etch rates per cycle were found to increase from 0.5 to 1.3 Å/cycle with process temperature increasing from 100 to 250°C. Transmission electron microscopy (TEM) studies conducted on ZnO-coated nanowires before and after ALE proved the isotropic character of the process. Moreover, the ALE process produced no surface damage/amorphization, as demonstrated by high resolution TEM inspection. *In-situ* infrared spectroscopy measurements were conducted to elucidate the mechanism underlying self-limited etching. Based on these measurements, a preliminary reaction mechanism is proposed in which Zn(acac)₂ is assumed to be the etching product and persisting acac-species on the ZnO surface provide the self-limiting character. Finally, a high etch selectivity over SiO₂ and HfO₂, and the possibility to extend the process to other oxides such as Al₂O₃ are also demonstrated.

We believe that this plasma-based ALE process represents a valuable addition to the ALE toolbox and opens-up new possibilities for using plasma-processing to achieve isotropic etch profiles. Furthermore, similar approaches can be used to extend the process to other materials, such as nitrides, by tuning the plasma chemistry accordingly.

(1) Lee, C. G. N. et al., The Grand Challenges of Plasma Etching: A Manufacturing Perspective. *J. Phys. D: Appl. Phys.* **2014**, *47*, 273001.

(2) Lill, T. et al., Directional Atomic Layer Etching. *Encycl. Plasma Technol.* **2016**, 133–142, Taylor & Francis.

(3) George, S. M. et al., Prospects for Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions. *ACS Nano* **2016**, *10*, 4889–4894.

4:45pm ALE2-MoA-14 Etching Reactions of Halogenated Layers Induced by Irradiation of Low-energy Ions and Gas-clusters, Kazuhiro Karahashi, T Ito, S Hamaguchi, Osaka University, Japan

In recent years, in microfabrication of various new devices such as MRAM, PRAM, RRAM, etc., damage-free, high-precision etching technologies of various materials are required. Some promising atomic layer etching processes use the formation of a halogenated layer on a metal surface and an adsorption layer of an organic molecule. If one uses ion irradiation to achieve etching anisotropic in atomic layer etching (ALE), it is necessary to reduce the incident ion energy and minimize damage formation to the surface. It is therefore important to understand surface reactions induced by low-energy ion irradiation. Similarly surface reactions by the irradiation of gas clusters or free radicals are also causes low or no damage to the surface. Therefore such processes may also be used for ALE.

In this study, fluoride layers formed on the surfaces of silicon, copper, nickel and cobalt were evaluated by exposure to XeF₂ using XPS. In addition, the process of removing fluoride layers by low energy ions and clusters was discussed. XeF₂ was exposed to the cleaned surface of the sample (Si, Cu, Ni, Co) and the chemical state of the surface layer after irradiation by *in-situ* photoelectron spectroscopy (XPS) was evaluated. The desorption reaction was evaluated by measuring changes in the surface fluorinated layer by irradiation with low-energy Ar ions (30, 50, 100 eV) and Ar cluster ions (3,000 atoms / ion, 3 keV / cluster). A fluoride layer with metal-fluorine bonds was formed on the surface by exposure to XeF₂. The fluoride layer formed on the Ni surface was almost saturated at 1000 L

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exposure. The adsorption process was a self-limiting process. The fluoride layer was removed by Ar⁺ ion irradiation with an energy of 30 eV. In this single step of ALE, the substrate surface was etched and the etched depth was limited to the depth of the fluoride layer.

5:00pm **ALE2-MoA-15 Optimization of Atomic Layer Etch Process for Fabrication of Dual Barrier GaN-based Power Device using *in-situ* Auger Spectrometric Surface Analysis**, Xu Li, H Zhou, K Floras, S Cho, D Hemakumara, D Moran, I Thayne, University of Glasgow, UK

ALE (Atomic Layer Etch) as a precisely etching technique removes very thin layers of materials has attracted extensive attentions in semiconductor processing, which is particularly suitable for fabricating GaN-based e-mode power devices in cascode module. For GaN-based power transistors employing a gate recess process, ALE has the potential to offer the etching precision required to precisely control device threshold voltage. In this work, an ALE process developed for etching group III nitrides in a dual barrier device materials consisting of a 2 nm GaN cap layer, a 4-8 nm InAlN barrier layer, another 1 nm GaN cap layer for the following 3 nm AlGaIn barrier layer above a 250 nm GaN channel and 4 μm C-doped buffer layer on Si wafer grown by MOCVD based on a cycled procedure of HBr bromination of the semiconductor surface followed by argon plasma removal of the modified surface layer has been optimized using *in-situ* Auger spectrometric analysis which supplies the information of the etching progress through different layers in the device materials via analyzing the surface composition during ALE processing.

A cluster tool from Oxford Instrument Plasma Technology has been used for ALE etching and *in-situ* analysis, which includes (amongst other process chambers and *in-situ* metrology) an inductively coupled plasma (ICP) etching chamber with repeat loop function, a basic requirement of an ALE process, and an Scienta Omicron NanoSAM surface analysis tool (including an Auger spectrometer). The clustered arrangement enables samples and wafers to be subjected to plasma processing before transfer into the analysis chamber under vacuum. The etching chemistry was based on the formation of self-limited Ga, In and Al bromides on the sample surface as a consequence of exposure to a short HBr gas pulse in the plasma etch chamber. This modified surface was then removed using an Ar plasma with an optimized RF power level which removes only the surface bromides and is not going to induce damage to the underneath materials. Etching could be suspended at any ALE steps in order to transfer the sample into analysis chamber to carry out Auger spectrometric analysis for determining which layer the etching was in. Experiments showed that the Auger spectrum could clearly and sensitively indicate the layer where the etching is going on, which is useful in fabricating e-mode transistors in the cascode module devices.

5:15pm **ALE2-MoA-16 ALE to Enable Memory Scaling**, Alex Schrinisky, C Huffman, M Koltonski, A Wilson, Micron

INVITED

Aggressive pitch scaling for both DRAM and non-volatile memory devices is pushing etch loading and precision control outside the limit of conventional continuous subtractive etch processing. Extreme control in removal and selectivity is required to enable forward looking devices. Atomic Layer Etching (ALE) techniques propose to achieve control at an atomic scale and could offer solutions to many of the key scaling challenges now faced by developers of next Gen IC's.

Atomic Layer Etching

Room Premier Ballroom - Session ALE-MoP

Atomic Layer Etching Poster Session

ALE-MoP-1 A Reliable Atomic Layer Etching Approach in Angstrom-level Flatness Control for Uniform CVD Grown TMDs Preparation, *Chao-An Jong*, National Nano Device Laboratories, Republic of China; *P Chiu*, NARL, Republic of China; *C Wang, M Lee*, National Taiwan Normal University, Republic of China; *P Chen*, Minghsin University of Science & Technology, Republic of China; *C Lin, C Hsiao*, NARL, Republic of China

Transition metal dichalcogenides (TMDs) has attracted considerable attention because of their tunable electrical and optical properties which is sensitive to their thickness. It is well known that the bandgap transitioned from direct to indirect when thickness increased [1-3]. The TMDs films usually obtained by exfoliated and CVD process are widely explored for different electronics and optoelectronic device fabrication. Although CVD process is announced for the large scale and continuous film preparation, it is still challenging to control the layer uniformity during the randomly nucleation and growth process. (Fig. 1)

A modified CVD process, which deposit precursor film on desired substrate and followed by the chemical reaction with chalcogens, is promising not only its potential for wafer scale synthesis but also the capability of a continuous, selective area synthesis and uniform layered TMDs formation. Lots of experimental data announced for the controllability between the precursor thickness and the numbers of TMDs layers [4-5]. However, it is very challenging for bottom-up growing film in angstrom level thickness and flatness control.

In this study, we propose a prospective application of atomic layer etch (ALE) process [6] in precursor film thickness and flatness control for uniform CVD grown TMDs preparation (Fig. 2). An ionic plasma source is equipped for thinning down. The ions were supplied from ionized Ar gas (99.9995%) with corresponding 380 W RF power, 300 V grid voltage, and 300 mA current. A set of radio frequency neutralizer (RFN) was used to prevent charge build-up on the substrate surface. By adjusting the RF power and the grid current/voltage, the thickness and flatness of precursor film can be well controlled.

The flatness of studied films are characterized by atomic force microscope (AFM). 10nm WO₃ film is prepared for etching. Followed by the sulphurization process, layered WS₂ films were also characterized by Raman and photoluminescence (PL) measurement. The root mean square (rms) roughness of as-deposited WO₃ film, etched WO₃ film and WS₂ film were taken. The rms data of etched WO₃ films are around 5Å ± 0.5Å within 80mm x 80mm scanned area (Fig. 3). The rms data for WS₂ film formed by sulfurizing etched WO₃ film are 4Å ± 0.5Å. The layer number of WS₂ film can be well identified by calculating Raman frequency difference between the in-plane (E_{12g}) and out-of-plane (A_{1g}) modes (Fig. 4). Compare to the PL spectrum, a specific number layer of high quality TMDs can be precisely synthesized. The approach is promising for wafer-scale, continuous and uniform TMDs film and stacking heterojunction p-n TMDs-based device fabrication.

ALE-MoP-2 Surface Cleaning of SiO₂ Layers by Atomic Layer Etching with Low Global Warming Potential Gases, *Yongjae Kim, T Cha, S Lee, Y Cho, H Chae*, Sungkyunkwan University (SKKU), Republic of Korea

When determining the yield and performance of semiconductor devices, controlling impurities and particles is important. Etching process generates many contaminants for instance native oxide, organic materials and inorganic materials. Among them, native oxide is considered critical one because it causes higher contact resistance. It can create higher contact resistance, which makes the IC inoperable. Other disadvantages of native oxide involve leakage current on gate oxide and inadequate formation of silicide in devices. [1] Typically wet cleaning processes are mainly applied to remove native oxide, but the processes are reaching the limits in high aspect ratio patterns in nanoscale and highly integrated devices. [2] Recently new dry-cleaning technology are being studied to overcome these problems of wet cleaning processes. [3] Many perfluorocarbon (PFC) such as CF₄, CHF₃, and C₄F₈ gases are widely used in semiconductor processes for etching and cleaning processes. PFCs are global warming gases and the have long lifetime. [4]

In this work, cyclic plasma process was studied for SiO₂ (native oxide) removal with surface modification in an inductively coupled plasma (ICP)

reactor with C₃F₇OCH₃, Ar, O₂ chemistries. The process consists of two steps of surface modification and removal step. In the first step, SiO₂ surface is modified with fluorocarbon polymers generated with C₃F₇OCH₃ having low global warming potential. In the second step the fluorinated oxide is removed with ions or radicals generated from Ar or O₂ plasma. Formation of fluorocarbon polymer layer on SiO₂ surface was confirmed by SEM and XPS analysis. Cleaning rate was investigated by varying bias voltage and ion density by monitoring the processes with a VI probe and an ion probe. It is also confirmed that the removal rate showed self-limited characteristics as the processing time increases. Removal rate were compared at various conditions of reaction gases and plasma power and the rate could be controlled under 10 Å/cycle.

References

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ALE-MoP-3 Electrical and Residual Gas Diagnostics of Pulsed Plasma Atomic Layer Etching in Silicon, *G Kwon, Hee Tae Kwon, W Kim, G Shin, H Lee*, Kwangwoon University, Republic of Korea

As the plasma etching process requires atomic-scale fidelity, Atomic Layer Etching (ALE) is now emerging. This is because conventional plasma etching causes various types of problems, for example, ARDE (Aspect Ratio Dependent Etch), and the feature size fabricated in the manufactures shrinks rapidly in nanoscale.

ALE has two kinds of method. The first is called as ALE, which is opposite to ALD. The second is called Quasi-ALE. This Quasi-ALE consists of several types, such as chemistry reaction, energy control, and flux control. With these two kinds of ALE method, ALE is steadily developing. By the way, there are not many diagnostics of ALE yet.

Therefore, we did plasma diagnostics qualitatively with introducing Quasi-ALE with energy control. Pulsed Plasma was used for tailoring plasma parameters, in order to achieve atomic layer etching of silicon in CCP (Capacitively Coupled Plasma) reactor. Both chlorine gas and argon gas were injected into the reactor for adsorption and desorption. For plasma diagnostics of ALE in silicon qualitatively, we used electrical probe to figure out low temperature (T_e). Also, RGA (Residual Gas Analyzer) was used to check by-products. All experiments were set with proper environment such as adequate pulse frequency and pressure, and so on.

ALE-MoP-4 Spontaneous Etching Behavior of Oxide and Sulfide Underlayers during Atomic Layer Deposition of Cu_{2-x}S using Cu(dmamb)₂ and H₂S, *J Han*, Seoul National University of Science and Technology, Republic of Korea; ***Raphael Agbenyeke***, University of Science and Technology, Republic of Korea

The rapid diffusivity of Cu⁺ ions in the hexagonal-close-packed crystal structure of Cu_{2-x}S is a trigger for many interesting and sometimes unexpected observations made during the growth of Cu_{2-x}S films. In this study, we present the etching of oxide and sulfide thin film underlayers during the atomic layer deposition (ALD) of Cu_{2-x}S, which is driven by the high diffusivity of the Cu⁺ ions. Although the infiltration of the underlayers by Cu⁺ ions plays an essential role in the etching process, it is suspected that the eventual etching behavior of the underlayer are strongly dependent on the lattice or bond dissociation energy of the underlayer materials. In the experiments, thin films of ZnS, ZnO, SnS, and SnO were etched to different degrees during ALD of Cu_{2-x}S. In contrast, SnO₂ exhibited a high resistance to etching. Interestingly, a selective removal of Zn²⁺ was observed when a ternary Zn_{1-x}Sn_xO film was used as underlayer. Based on X-ray spectroscopy results, and the results from other supplementary experiments, we proposed a possible reaction mechanism for the etching process. Finally, the etching phenomenon was extended to the synthesis of Cu_{2-x}S nanowires, which have the potential of being used as absorber materials for photovoltaic cells.

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ALE-MoP-5 The Phenomenon of Reduction on the Austenitic Stainless Steel Affected Hydrogen Species into the Screen Plasma Technology, Jongdae Shin, Korea Institute of Industrial Technology(KITECH) and Inha University, Republic of Korea; *S Kim,* Korea Institute of Industrial Technology(KITECH), Republic of Korea

Although austenitic stainless steel has excellent corrosion resistance, it has low applicability due to low hardness. Therefore, various surface hardening treatments have been developed. Especially, plasma nitriding process has been under various researches due to its environment and easy applicability. However, if the oxide film of the material cannot be uniformly removed, it is difficult to secure a uniform nitride layer during the nitriding process. There were discussions about the role of high-energy hydrogen species to understand the principle of oxide film removal which arising from laser ablation, microwave assisted non-thermal hydrogen plasma, and ion implantation technology. Generally, H α (656.28nm, 1.89eV), which is a hydrogen species generated by glow discharge, is characterized by the fact that the surface reduction of the Austenitic stainless steel becomes very uneven due to its reaction energy. On the other hand, in the case of the plasma by the screen plasma technology, high-energy and high-density hydrogen species can be generated by adjusting the degree of vacuum, current, and gas mixture. Through this, it was judged that intense physical-chemical reaction and a uniform reduction reaction occurs inside the chamber. Hydrogen species due to high energy generation are predicted to be about H β (486.1 nm, 2.55 eV), H γ (434.1 nm, 2.86 eV), which occurs depending on the parameters in the screen plasma apparatus. The state of the hydrogen active species was observed through OES (Optical Emission Spectroscopy). At this time, the state of the energy and the ion density were analyzed through the Langmuir probe to closely diagnose the plasma state. After that, the relevant facts was studied by analysis using contact angle measurement, Auger Electron Spectroscopy, and Glow Discharge-Optical Emission Spectroscopy of the oxidation-reduction on the surface.

ALE-MoP-6 Fabrication of GaSb Mesa Structures by Atomic Layer Etching using Trisdimethylaminoantimony, Katsuhiko Uesugi, H Fukuda, Muroran Institute of Technology, Japan

We investigate atomic layer etching (ALE) of GaSb dot structures using trisdimethylaminoantimony (TDMASb) precursor to fabricate GaSb mesa structures. Self-assembled GaSb dots have been grown on GaAs(001) substrates at the temperature of 480-520°C by using metal-organic molecular beam epitaxy (MOMBE). At 480°C, GaSb quantum dots (QDs) with 8 nm-height and 70 nm-width were grown in Stranski Krastanow mode. Then the GaSb QD surfaces were etched by the reaction with TDMASb at the substrate temperature of 480°C. At the initial stage of GaSb QD etching, the dot diameter has not been changed. However, the height reduction of dots was observed with increasing of TDMASb supply. The GaSb QDs after 90 s etching showed the truncated pyramidal shape and the average height and width of them were 4 nm and 70 nm, respectively. All GaSb QDs were etched by the TDMASb supply for 140 s, and the surfaces was changed to atomically flat (1x3) surfaces. This result indicates that the ALE process of GaSb QDs using TDMASb primarily causes the decrease in dot height. The etching reaction was promoted at the top (001) facet in comparison with the other facets of dot side.

The submicron-sized GaSb dots were also grown at 520°C. The height and width of GaSb submicron dots (SDs) were 100 nm and 350 nm, respectively. Self-size-limiting phenomenon of dome-shaped GaSb SDs depend on temperature was clearly observed. After ALE of GaSb SDs, GaSb mesa structures were fabricated by the TDMASb supply for 30 s at 450°C. The GaSb mesa structures were found to be laterally surrounded by (111) and (110) facets together with circular (100) facet at a convex curved region. The diameter of circular (100) facet was 120 nm. These results suggest that the size and facets of GaSb mesa structures can be controlled by using ALE technique with TDMASb.

ALE-MoP-7 Interaction of Hexafluoroacetylacetone (HFAC) Molecules with Nickel or Nickel Oxide Film Surfaces for Atomic Layer Etching (ALE) Applications, Abdulrahman Basher, M Isobe, T Ito, K Karahashi, S Hamaguchi, Osaka University, Japan

Magnetic Random Access Memories (MRAMs) are one of the most promising nonvolatile memories. Manufacturing MRAM devices with nano-scale dimensions is still a challenge due to the difficulties in nano-scale patterning of magnetic tunnel junction (MTJ) stacks which are used in MRAMs to store data [1]. An MTJ stack consists of two ferromagnetic layers separated by a dielectric barrier layer. Therefore, the development of controllable etching processes in the range of nanometer scales is required with high anisotropy and low damage for magnetic materials. Organic

etchants may be used to establish low-damage and highly controlled etching processes [2]. Hexafluoroacetylacetone (hfac) has proved its efficiency for the use in dry etching of several materials such as semiconductors, minerals, as well as magnetic materials [1-4]. It has been found experimentally that nickel hexafluoroacetylacetonate Ni(hfac)₂ can be formed when gas-phase hfac is exposed to a pre-oxidized nickel (Ni) surface and the surface temperature is increased, which suggests the etching of Ni takes place under such conditions. On the other hand, when a clean Ni metal surface is exposed to hfac, hfac tends to break down and no Ni atom seems to desorb from the surface. The goal of this study is therefore to understand the interaction of an hfac molecule with a Ni or nickel oxide (NiO) surface and to evaluate the feasibility of hfac dry etching processes for metallic Ni and NiO films. In this study, quantum mechanical (QM) numerical simulation analysis is performed with Gaussian 09 to evaluate chemical reactions of hfac with Ni metal and NiO. It has been found that a decomposition of an hfac molecule can be energetically preferred when an hfac molecule is placed on a metallic Ni surface whereas an hfac molecule can be stably adsorbed on a NiO surface.

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ALE-MoP-8 Cost Effective Plasma Generation with High Efficiency and Reliability for Remote Plasma Removal Process: Magnetic Induction Plasma Source, Tae Seung Cho, S Park, D Lubomirsky, Applied Materials

Remote plasma removal process is playing an importance role in material removal with high selectivity in 3D structures of semiconductor. In remote plasma removal process system, the wafer process regime is completely isolated from plasma source by perforated metal plate such as showhead. The charged particles as well as radicals are generated by electrical discharge and only the radicals could pass through the perforated metal plate. In the wafer process regime, certain radical species reacts only with the material to be removed from the wafer while there's no reactions with any materials on the wafer. Since the charged particles are screened by the plate, the damages by energetic charged particles can drastically be reduced. Therefore, efficient radical generation with higher dissociation rate and less charged particle leakage to wafer process region could dramatically promote the performance of remote plasma removal process.

Magnetic induction plasma concept is being used for lighting bulbs as well as Tokamak fusion reactor for several decades (Fig.1). Especially, the magnetic induction lighting and its driving electronics is being optimized for many years. Since the magnetic induction lighting doesn't have any electrode inside the bulb there's no particles from the electrode sputtered by energetic ions. In addition, magnetic induction plasma source as an inductively coupled plasma has higher dissociation rate compared to typical capacitively coupled plasma. Thus, introducing the magnetic induction lighting and its driving technologies to remote plasma removal process would make removal process more efficient and reliable with reduced cost of ownership.

Prototype chamber for magnetic induction plasma source for remote plasma removal process has been simply assembled with standard KF flanges of elbows and crosses that could be brought off the shelf (Fig.2). The commercial electronic ballast for magnetic induction lighting bulb has been used to generate the plasma inside the chamber. The control circuit to make the plasma stable by modulating the power and frequency (0-400Wmax and 200-400kHz) has been added to the ballast. For preliminary study, Ar+N₂ plasma has been successfully generated in the chamber by using the ballast with wide operating pressure ranges from 50mTorr to 200Torr (Fig.3). Based on OES study, it has been confirmed that emission intensity from argon increases with increasing power from 47W to 120W (Fig.4) and will be further confirmed that remote plasma removals of material increases with power.

Monday Afternoon Poster Sessions, July 30, 2018

ALE-MoP-9 A Study of InGaAs Nanowire Fabrication by Atomic Layer Etching, Doo San Kim, J Park, W Lee, G Yeom, Sungkyunkwan University (SKKU), Republic of Korea

Atomic layer etching (ALE) is a next generation etching technique consisting of cyclic removal of monolayer by repeating adsorption and desorption, and it is suitable for nanoscale semiconductor device fabrication due to the layer-by-layer control and minimizing the surface damage of the materials. So far, the ALE methods have been studied by many researchers on various semiconductor materials. Among these materials, III-V semiconductor compounds such as indium gallium arsenide (InGaAs) can be applied to 3-dimensional structure nanodevices such as nanowire field effect transistors due to a great electrical characteristics than silicon-based devices.

In this study, InGaAs nanowire was fabricated with a 50 nm-line patterned polystyrene (PS) as a etch mask which was formed using a nano-imprint lithography (NIL) technique. For InGaAs ALE, chlorine was used as the adsorption gas and, for desorption, a low-energy Ar⁺ ion beam was used to remove the chlorine chemisorbed InGaAs on the surface. Using an optimized ALE conditions, the InGaAs was etched and the PS mask remained on the InGaAs surface was removed by oxygen-ICP plasmas, and the fabricated InGaAs nanowires were observed by Field emission-secondary electron microscope (FE-SEM). After the fabrication of InGaAs nanowires, the properties of InGaAs nanowires were investigated and compared with those fabricated with conventional reactive ion etching methods.

ALE-MoP-10 Chrome Atomic Layer Etching, Jin Woo Park, D Kim, W Lee, G Yeom, Sungkyunkwan University (SKKU), Republic of Korea

The uniformity of the critical dimension (CD) of the photomask is important for the nanoscale high-intergraded circuits (ICs) for the fabrication of next-generation semiconductor devices. The photomask is generally consisted of quartz, chrome (Cr), and molybdenum silicon oxynitride (MoSi). Depending on the type of photomasks such as standard chrome on glass (COG), opaque MoSi on glass (OMOG), and phase-shifting mask (PSM), Cr is dry-etched and the Cr is used as a hard mask to fabricate the photomask due to the low-etch selectivity between MoSi and quartz. Thus, the dry etch process of Cr with a low surface damage (such as low LER and low LWR) and high-uniformity plays an important role in determining the CD of the photomask.

Atomic layer etching (ALE) technology can be used as a exquisite process at the atomic level with a high-uniformity and low-defect density of surface regardless of plasma uniformity during the semiconductor manufacturing process, and is attracting attention as an etching technique for next-generation semiconductor fabrication of nanoscale. In this study, the ALE characteristics of Cr have been investigated using O₂ or Cl₂/O₂ for adsorption and Cl₂ or Ar ion beam for desorption, respectively, during the etch cycle to control the etch depth precisely and to minimize the surface damages of Cr. Also, the monolayer removal mechanism of Cr was investigated by X-ray Photoelectron Spectroscopy (XPS). By using ALE, the controlled Cr etch depth per cycle and very high-etch selectivity of Cr over various Si-based materials such as silicon, silicon dioxide, and silicon nitride etc. in addition to minimized surface damage could be obtained.

ALE-MoP-11 MoS₂ Lateral-Heterojunction Device Using Atomic Layer Etching, Ki Seok Kim, Y Ji, K Kim, G Yeom, Sungkyunkwan University (SKKU), Republic of Korea

Molybdenum disulfide (MoS₂) has been intensively investigated because of its unique properties in various electronic and optoelectronic applications. More specifically, as the layer is reduced from bulk to bilayer and monolayer, the band structure changes from indirect to direct at the K point of the Brillouin zone, and the band-gap also changes from 1.2 to 1.9 eV. Accordingly, the technology involved in controlling the MoS₂ layers is very important in various nano-device applications. To control the MoS₂ layers, atomic layer etching (ALE) (1st step: radical adsorption / 2nd step: reacted compound desorption) can be a highly effective and precise technique while avoiding damage and contamination that can occur during the etching. In this study, for the MoS₂ ALE, the Cl radical is used as the adsorption species and a low-energy Ar⁺ ion is used as the desorption species. In addition, mono-/bi-layer lateral-heterojunction device was fabricated using ALE technique after PR patterning of bilayer MoS₂. The results showed that the photocurrent was increased in heterojunction regions due to the difference in work function and electron affinity between mono-/bi-layer MoS₂. The photocurrent is increased because the exciton generated in the monolayer MoS₂ is thermally diffused into the bilayer MoS₂ region and the additional carrier is generated. Therefore, the

lateral-heterojunction 2D device fabricated using ALE technique can be a very important device that can be applicable to next-generation nanosensor devices.

ALE-MoP-12 Study of Atomic Layer Etching (ALE) of SiO₂ Using Inductively Coupled Plasma (ICP) Etch Chambers with Multi-chamber or Multi-step Approach, Shuang Meng, S Ma, Mattson Technology, Inc.

Atomic layer etching (ALE) of SiO₂ has been traditionally done with a fluorocarbon deposition followed by Ar and/or O₂ plasma activation per etch cycle. However, the resultant etch per cycle (EPC) and across-wafer uniformity are strongly affected by CF_x deposition condition, and to a lesser degree, the plasma activation condition. In this report we studied the impact of CF_x gas species (CF₄ vs. CHF₃), gas composition (Ar/N₂/Forming gas), adsorption kinetics (thermal vs. radical), adsorption pressure and temperature, as well as plasma activation conditions (Ar vs. O₂) on ALE etch characteristics and across-wafer uniformity using Mattson's 300mm Aspen III platform. This platform includes two ICP chambers with vacuum transfer capability in-between, one chamber being a ICP plasma asher which can be used for CF_x deposition at relatively high temperature and high pressure, and the other one being a low-temperature low-pressure etcher that performs radical and ion bombardment. Alternatively, the CF_x deposition can also be performed in the etcher at low temperature and low pressure followed by *in-situ* plasma activation. This system allows independent controls of CF_x deposition conditions and the subsequent plasma activation conditions.

Our results show that SiO₂ removal rate and across-wafer uniformity are largely affected by CF_x adsorption temperature and pressure as well as mixing gas species, and less dependent on CF_x molecule type. Adsorption of CF_x at higher temperature and higher pressure gives lower EPC compared to adsorption at low temperature and low pressure. In addition, Ar plasma activation results in higher EPC than O₂ plasma activation which has additional effect of removing residue carbon from the oxide surface. Across-wafer uniformity can be effectively tuned by controlling the amount of Ar injected during the CF_x deposition steps.

ALE-MoP-13 Tuning Etching Characteristics of Plasma-Assisted ALE of SiO₂ via Hydrocarbon Precursors, Ryan Gasvoda, Colorado School of Mines; S Wang, E Hudson, Lam Research Corp.; S Agarwal, Colorado School of Mines
Due to ever decreasing device dimensions and the introduction of 3D device architectures, it is challenging to operate within a narrow processing window using conventional plasma etching. One method to address the demands of the next-generation of devices is atomic layer etching (ALE) which provides high fidelity, selectivity, directionality, and layer-by-layer removal. Plasma-assisted ALE has been extensively studied for a variety of materials, including Al₂O₃, HfO₂, Si, and Si-based dielectrics. Plasma-assisted ALE of SiO₂ typically uses two sequential steps in a cyclic fashion: CF_x deposition from a C₄F₈/Ar plasma followed by an Ar plasma activation step. ALE of SiO₂ has been demonstrated to remove ~4 Å per cycle. It is proposed that broader control of the surface reactions and etching characteristics can be achieved by introducing an additional reactant.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions, film composition, as well as the net film thickness. To controllably alter the EPC, we introduce a hydrocarbon precursor into the reactor prior to the CF_x deposition step. This precursor reacts with the surface Si-OH groups leaving a SiO₂ surface terminated with hydrocarbons. An infrared spectrum of the surface shows that the hydrocarbon precursor is resistant to the C₄F₈/Ar plasma. After the Ar plasma activation step, a broad increase from ~1230 – 1800 cm⁻¹ indicates that a graphitic hydrofluorocarbon film accumulates on the surface. This graphitic hydrofluorocarbon film prevents the complete activation of the CF_x film during the Ar plasma step, thus resulting in a lower EPC than the baseline ALE process. This modulation of etch properties may have applications for controlling etch selectivity.

The hydrocarbon precursor consists of two different groups: the hydrocarbon backbone and reactive head group. Changing the reactive head group leads to different surface coverage on the Si-OH terminated SiO₂ film and thus a different EPC. In this poster, two different classes of hydrocarbon precursors (aminosilanes and acid chlorides) are screened for surface coverage, EPC reduction, and surface composition after the Ar plasma activation step. The length and structure of the hydrocarbon chain are also discussed.

Monday Afternoon Poster Sessions, July 30, 2018

ALE-MoP-14 Modeling and Simulation of *in-situ* Cleaning Sequence Using NF₃/NH₃ Remote Plasma, Romel Hidayat, T Mayangsari, J Gu, H Kim, Sejong University, Republic of Korea; Y Kwon, Kyung Hee University, Republic of Korea; J Jung, W Lee, Sejong University, Republic of Korea

In semiconductor manufacturing processing, the removal of native oxide on the silicon surface is one of the critical issues to obtain low contact resistance. Although wet cleaning process using a dilute HF solution is the most widely used method for oxide removal, it cannot completely prevent the formation of native oxides because the wafer is exposed to air before being loaded into the selective epitaxial growth chamber or metal deposition system. Siconi™ cleaning process based on NF₃/NH₃ remote plasma was successfully employed as pre-Ni Silicide cleaning at 65 nm and showed lower junction leakage [1]. This process is composed of two steps, the fluorination of silicon oxide by a remote plasma of NH₃/NF₃ at near room temperature and the sublimation of fluorinated layer by annealing at 180°C. Understanding the detailed reaction mechanism underlying the cleaning process will lay a foundation for developing new atomic layer cleaning processes. The reaction mechanism was proposed [1], however, more experimental evidences are needed, and more detailed mechanisms have not yet been elucidated. In this study, we modeled and simulated the Siconi™ process by density functional theory (DFT) and molecular dynamics (MD) calculations. The fluorination of oxide was simulated by introducing HF and NH₄F on OH- or F-terminated SiO₂ surfaces by DFT, and the sublimation process was simulated by MD-annealing. We found the fluorination process is limited by forming the SiF₆(NH₄)₂ salt on the surface, showing that NH₄F is the key molecule for the *in-situ* cleaning process.

Keyword: *simulation, remote plasma, siconi, density functional theory, molecular dynamic*

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ALE-MoP-15 Biological Characteristics and Antibacterial Performance of Tantalum Oxide and Zinc Oxide Thin Films, Yin-Yu Chang, National Formosa University, Republic of China; H Huang, China Medical University, Republic of China; M Tsai, Hungkuang University, Republic of China; Y Lin, National Formosa University, Republic of China

The surface modification of biomaterials with better biocompatibility and antibacterial feature has been a challenge for many years. Tantalum oxide (Ta_{1-x}O_x) and zinc oxide (ZnO) thin films have been used as the material of orthodontic and dental implants due to their impressive biocompatibility, corrosive resistance, and antibacterial activity on the microorganisms. Among the surface engineering techniques, atomic layer etching (ALE) and plasma electrolytic oxidation (PEO) are rising technologies which can produce unique surface for cell adhesion and improve the biocompatibility for further implantation. In previous studies, thin films of Ta₂O₅ and ZnO have been found to show both the antibacterial ability and biocompatibility in vitro. In this study, a pre-treatment of surface modification on titanium (Ti) substrates has been made by ALE and PEO. Porous oxide layers formed, and a series of Ta, ZnO, and Ta₂O₅ and ZnO films were then deposited onto the porous surface of Ti substrates by using a twin-gun high power impulse magnetron sputtering system. The surface morphology, crystal structure, and bonding state of the films were identified by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). To evaluate the antibacterial ability, *Staphylococcus aureus* (*S. a.*, Gram-positive bacteria) and *Actinobacillus actinomycetemcomitans* (*A. a.*, Gram-negative bacteria) were tested. *S. a.* and *A. a.* were the main origins of infection mostly occurred in clinical orthopedic/oral implants, and both of these two types of bacteria were tested by a fluorescence staining method (Syto9) and bacterial viability agar tests. The in vitro cytotoxicity was tested followed by the standard of ISO 10995-5:2009. Cell viability and proliferation of human osteosarcoma cell line (MG-63) and human skin fibroblast (SKF) cells cultured on these films were also determined by using the MTT assay. The result showed that an appropriate ALE/PEO pre-treated Ti with Ta₂O₅ and ZnO thin films improved both the antibacterial ability to *A. a.* and *S. a. bacteria* and biocompatibility to SKF and MG-63 cells in vitro.

ALE-MoP-16 *In situ* Quantitative Analysis of Chlorine Adsorption on Ion-irradiated GaN for Atomic Layer Etching, Masaki Hasegawa, T Tsutsumi, H Kondo, K Ishikawa, M Hori, Nagoya University, Japan

Gallium nitride (GaN) is a candidate material for fabrication of the next-generation power electronic devices. To realize the GaN devices, atomic level control of etching of GaN is necessary. Thus, atomic layer etching (ALE) technique of GaN was suggested by cyclic processes of Ar ion exposure and Cl adsorption onto GaN. For precise control, we issues on variations of atomic level removal of GaN-Cl by-products, that is, the ion

bombarded GaN surface varies on both Ar ion-energy and Cl-flux for the adsorption. Therefore, we are focusing on Ar and Cl reactions with GaN and have elucidated Cl adsorption on the Ar ion bombarded GaN surface using the beam experiments with *in situ* X-ray photoelectron spectroscopy (XPS), as developed previously.[1,2]

Sample is the GaN grown on sapphire by Hydride Vapor Phase Epitaxy (HVPE) method. After wet cleaning (5% HF), native oxide on GaN surface was removed by Ar ion sputter. Subsequently, Cl radicals generated in Cl₂ gas (flow rate 0.5 sccm) plasma by application of RF power of 400 W were exposed to the sample surface with a dosage of 10¹⁹ cm⁻². Sequentially, Ar ions generated in Ar gas (flow rate 1.0 sccm) plasma by application of RF power of 400 W were exposed to the sample surface with accelerating voltage of 200 V and a dosage of 10¹⁶ cm⁻². At each treatment, we observed the sample surface by *in situ* XPS method.

After GaN surface was irradiated by Ar ions with accelerating voltage of 200 V and a dosage of 2×10¹⁶ cm⁻², the surface was formed by a Ga rich layer with a thickness of approximately 0.8 nm stacked on a 0.2-nm-thick amorphous layer (a-GaN). After Cl radicals were exposed with a dosage of the order of 10¹⁹ cm⁻², the Ga rich layer was removed selectively and a mixing layer of Ga-N-Cl was formed with almost similar thickness of 0.8 nm in the a-GaN layer. For the ALE of GaN, parameters such as ion energy, etchant fluxes, and surface reactions play an important role for atomic control of stoichiometric removal of GaN.

Acknowledgement the authors thank to Mr. A. Tanide of the SCREEN holding Co., Ltd. for fruitful discussion.

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Atomic Layer Etching

Room 104-106 - Session ALE1-TuM

ALE: Gas-phase and/or Thermal ALE

Moderators: Steven M. George, University of Colorado at Boulder, Venkat Pallem, Air Liquide

8:00am **ALE1-TuM-1 Fluorocarbon-based Atomic Layer Etching of Silicon Dioxide in Conventional Plasma Tools**, *Stefano Dallorto*, Lawrence Berkeley National Laboratory; *A Goodyear*, M Cooke, Oxford Instruments Plasma Technology, UK; *S Dhuey*, A Schwartzberg, Lawrence Berkeley National Laboratory; *C Ward*, Oxford Instruments Plasma Technology; *I Rangelow*, Ilmenau University of Technology, Germany; *S Cabrini*, Lawrence Berkeley National Laboratory

Controlling Ångstrom-thick film etching is essential for further development of sub-10 nanometer semiconductor manufacturing. The atomic scale era requires the use of decreasing film thickness together with stringent surface property control: preventing material damage and controlling over etching directionality and material selectivity.

Single digit nanofabrication requires the ability to achieve atomic scale etching control and material selectivity during pattern transfer. Atomic Layer Etching (ALE) satisfies these needs as critical dimensions continue to shrink. An ALE process consists of two sequential steps: A) surface modification: a thin reactive surface layer with a well-defined thickness is created B) layer removal: the modified layer is more easily removed than the unmodified material.

Here we study a Fluorocarbon(FC)-based ALE process using Ar plasma and CHF_3 gas for controlling the etching of silicon dioxide at the atomic level. During the saturative surface reaction, CHF_3 is injected in the steady state Ar plasma. CHF_3 breaks and forms some fluorocarbon polymer on the SiO_2 surface. CHF_3 is then purged from the chamber and FC polymer is a source of fluorine, which reacts with SiO_2 modifying its surface. For low energy Ar^+ ion bombardment conditions, the physical sputter rate of the substrate vanishes, whereas the modified surface can be etched when FC reactants are present at the surface.

With the goal of achieving high selectivity FC-based ALE, we first investigated the etching per cycle (EPC) using spectroscopic ellipsometer on unpatterned surfaces. Using CHF_3 -based ALE for SiO_2 etching, we proved ALE self-limiting behavior with etching rate of 6 Å/cycle. Figure 1 in Supplement shows SiO_2 features varying the ion power during the removing step (which decrease moving left to right) etched using different masks: ZEP and Chromium. Using a Cr mask (Figure 1: Row 2) the EPC is similar to the one of flat surfaces. Instead, SiO_2 features using ZEP mask (Figure 1: Row 1) have an EPC 50% higher than expected. Polymer mask (ZEP) is a source of carbon, hydrogen and oxygen, which interfere with the etch process bringing it out of the self-limiting window. SiO_2 features etched using lower DC bias (17 V) are aspect-ratio independent and results in a low degree of physical/ionic etching.

A successful application of the FC-ALE approach has been demonstrated. Overall, the cyclic CHF_3/Ar etch has proven to pattern features well with an hard mask, with great potential for significant improvement in overall etch performance.

8:15am **ALE1-TuM-2 Damaged Layer Control for Atomic Level Processes**, *Masanaga Fukasawa*, *T Tatsumi*, Sony Semiconductor Solutions Corp., Japan

INVITED

Atomic layer etching (ALE) is one of the most attractive methods for overcoming the limitations of conventional processes. One of the advantages of ALE is low-damage etching. However, it is impossible to stop plasma-induced damage from occurring because ions, radiation, and radicals are irradiated on a surface simultaneously. In the case of low-energy incidences of ions ($\sim 50\text{eV}$), the effect of radiation and radicals also has an impact on damage generation. In this presentation, I review the results of ion/radiation damage analysis.

Suppression of Si substrate damage caused by energetic ion bombardment is one of the most critical issues in advanced devices. The threshold energy for atomic displacement (E_d) of bulk Si crystal is reported to be 10-30 eV. When we use ion energy higher than the E_d , it is possible to generate damages in Si substrate. Si substrate damage during gate electrode etching causes a "Si recess" structure to form, which is reported to degrade device performance. Although the damage basically consists of a surface oxidized layer and underlying dislocated Si, the damage structure strongly depends

on the incident ion species, ion energy, and oxidation during air and plasma exposure. As both the Si recess and remaining dislocated Si degrade electrical performance, precise control of incident ion energy is indispensable to minimize damage generation.

We also found that photons with longer wavelengths than optical bandgap energy could reach the underlying dielectrics/Si interface and cause interface damage. UV radiation transmitting through the upper dielectrics could cause the electrical characteristics of underlying MOS devices to fluctuate. Thus, we must control VUV/UV radiation from plasma, even in the case of ALE processes.

ALE is one of the pulsed plasma, so we investigated an effect of transient behavior of a pulse modulated inductively coupled plasma on the photon-induced interface defects. The time-resolved OES revealed that the optical emission overshoot appeared after ignition because of the variation of the electron temperature and number density in the early ON phase. As a result, the amount of UV radiation damage increased compared with CW plasma. Thus, control of transient behavior is essential for reducing photon-induced damage in pulsed plasma.

The key challenges of atomic level processes for plasma-induced damage reduction are almost same as CW plasma. The effects of VUV/UV radiation and radicals become particularly apparent in the case of low-energy incidences of ions. In addition, the control and the monitoring of the transient behavior of pulsed plasma become more important for atomic precision etching.

8:45am **ALE1-TuM-4 Selective Thermal Cyclic ALE of Lanthanum Oxide via Formation and Desorption of Organo-lanthanum Complex**, *Yoshihide Yamaguchi*, *K Shinoda*, *S Fujisaki*, Hitachi R&D Group, Japan; *Y Kouzuma*, *S Sakai*, *K Kawamura*, *M Izawa*, Hitachi High-Technologies Corp., Japan

The demand for atomic layer/level etching (ALE) is increasing as the geometries of semiconductor devices continue to shrink. Remarkable progress has been made in the recent years to meet the enhanced requirements for a variety of materials to be atomically etched. One approach for selective isotropic ALE is rapid thermal cyclic ALE, which is cyclic repetitions of a self-limiting surface modification and a thermal desorption. Rapid thermal cyclic ALE of SiN, TiN, and W was developed by the authors [1, 2]. As for high-k lanthanum oxide (La_2O_3) whose boiling point is more than 4000°C , thermal etching via a low temperature ($< 250^\circ\text{C}$) volatile organo-lanthanum complex has also been developed [3], although the cyclic process has yet to be confirmed.

In this work, we present thermal cyclic ALE of La_2O_3 exposed to a mixture of a ketone-based ligand and a stabilizer followed by a thermal annealing. Our preliminary cyclic experiments on powdered La_2O_3 demonstrated that the mass of the powder sample decreased as the number of repetition cycles increased. In one cycle of chemical exposure and annealing, the average loss in mass was 0.074 mg, which corresponds to about 30 nm/cycle for a La_2O_3 film.

Formation of an organo-lanthanum complex was quasi-self-limiting because the change in the mass of the powder sample had shown saturation behavior. The volatile organic species in preliminary experiments were collected and spectroscopically analyzed. The resultant data was identified as an organo-lanthanum complex bearing a ligand moiety and a stabilizer moiety.

Next, we examined the effect of temperature during the chemical exposure. In this experiment, both La_2O_3 and SiO_2 films deposited on silicon substrates were used as sample materials. Substrate temperatures during the chemical exposure were 140°C and 260°C . The films' thicknesses were evaluated by scanning electron microscopy after the exposure. Because the etching of the La_2O_3 film was not detected when the temperature was 140°C , we concluded that the formation of the organo-lanthanum complex is self-limiting. On the other hand, continuous etching of the La_2O_3 film was observed when the temperature was 260°C , at which point the organo-lanthanum complex was volatile. The etching of SiO_2 was not detected at both temperatures. From these findings, we concluded that selective, thermal cyclic ALE of lanthanum oxide was successfully demonstrated.

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9:00am **ALE1-TuM-5 Thermal Atomic Layer Etching of Silicon Using an Oxidation and "Conversion-Etch" Mechanism, Aziz Abdulgatov, S George, University of Colorado - Boulder**

The thermal atomic layer etching (ALE) of silicon was performed using an oxidation and "conversion-etch" mechanism (see Supplemental Figure S1). In this process, the Si surface is oxidized to a silicon oxide layer using O₂ or ozone. The silicon oxide layer is converted to an Al₂O₃ layer using trimethylaluminum (TMA). The Al₂O₃ layer is fluorinated by HF to an AlF₃ layer prior to the removal of the AlF₃ layer by ligand-exchange using TMA. Si ALE was studied using silicon-on-insulator (SOI) wafers in a warm wall reactor with a hot sample stage. *In situ* spectroscopic ellipsometry was employed to monitor the thickness of both the silicon and the silicon oxide layer during Si ALE. These studies observed that the silicon film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant.

Using an O₂-HF-TMA reaction sequence, the Si ALE etch rate was 0.4 Å/cycle at 290°C (see Supplemental Figure S2). This etch rate was obtained using static reactant pressures of 250, 1.0 and 1.0 Torr, and exposure times of 10, 5 and 5 s, for O₂, HF and TMA, respectively. Reducing the O₂ pressure below 250 Torr reduced the etch rate. A lower etch rate of 0.2 Å/cycle at 290°C was observed at an O₂ pressure of 30 Torr. The order of the reactant sequence affected the Si etch rate. Changing the reactant sequence from O₂-HF-TMA to O₂-TMA-HF reduced the etch rate from 0.4 to 0.2 Å/cycle at 290°C. Comparable etching rates were observed using ozone instead of O₂ as the oxidant. Using an O₃-HF-TMA reaction sequence, the Si ALE etch rate was 0.5 Å/cycle at 290°C. The Si ALE etch rate decreased with process temperature for both the O₂-HF-TMA and O₃-HF-TMA reaction sequences. An oxide thickness of ~10-20 Å remained after Si ALE at 290°C. However, this oxide thickness could be removed by sequential TMA and HF exposures without influencing the underlying silicon film.

This new thermal Si ALE process is expected to yield isotropic etching. Thermal Si ALE will complement the plasma Si ALE process based on directional Ar⁺ ions that yields anisotropic etching. Thermal Si ALE should be useful in advanced semiconductor fabrication. Thermal Si ALE could also be utilized for atomic-scale polishing and cleaning of silicon surfaces. In addition, there may be applications in other areas such as silicon-based optoelectronics, photonics and MEMS fabrication.

9:15am **ALE1-TuM-6 Rapid Atomic Layer Etching of Al₂O₃ using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum with No Purging, David Zywotko, University of Colorado - Boulder; J Faguet, TEL Technology Center, America, LLC; S George, University of Colorado - Boulder**

An increase in Al₂O₃ atomic layer etching (ALE) rates versus time was demonstrated using sequential, self-limiting exposures of hydrogen fluoride (HF) and trimethylaluminum (TMA) as the reactants with no purging. The normal purging expected to be required to prevent chemical vapor etching (CVE) or chemical vapor deposition (CVD) is not necessary during Al₂O₃ ALE. The purgeless, rapid atomic layer etching (R-ALE) was studied from 250°C to 325°C using various techniques.

In situ quartz crystal microbalance (QCM) measurements monitored Al₂O₃ R-ALE at 300°C. The Al₂O₃ R-ALE process produced linear etching versus number of R-ALE cycles. The net result of fluorination by HF and ligand-exchange with TMA was a mass change per cycle (MCPC) of -32.1 ng/cm² using sequential, 1 s exposures for both HF and TMA with no purging. This mass change equates to a thickness loss of 0.99 Å/cycle or 0.49 Å/s. The Al₂O₃ R-ALE etch amount per cycle at 300°C was nearly equivalent to the previously measured Al₂O₃ ALE etch amount per cycle at 300°C using 30 s purge times. However, the Al₂O₃ R-ALE etch rate versus time at 300°C was 78 times faster than the previously measured Al₂O₃ ALE etch rate versus time at 300°C using 30 s purge times. *Ex situ* spectroscopic ellipsometry (SE) and XRR measurements also revealed temperature-dependent etch rates for Al₂O₃ R-ALE from 0.02 Å/cycle at 270°C to 1.12 Å/cycle at 325°C.

Additionally, patterned SiO₂ wafers were used to compare Al₂O₃ R-ALE and normal Al₂O₃ ALE with purging in high aspect ratio structures. Scanning electron microscope (SEM) images revealed that the etching was uniform for both processes and yielded comparable etch rates per cycle in the high aspect ratio structures. The HF and TMA precursors were also intentionally overlapped by various amounts to explore the behavior when both precursors are present at the same time. Similar to atomic layer deposition (ALD), where precursor overlap produces chemical vapor deposition (CVD), precursor overlap during Al₂O₃ ALE leads to AlF₃ CVD. However, any AlF₃ CVD growth that occurs during precursor overlap is removed by spontaneous AlF₃ etching during the subsequent TMA exposure. This

spontaneous AlF₃ etching by TMA explains why no purging is necessary during R-ALE.

9:30am **ALE1-TuM-7 Self-limiting Thermal Atomic Layer Etching of Tungsten Metal Using O₂ Oxidation and WCl₆ or WF₆: Role of Halogen Species in Temperature Dependence of ALE Reaction Rate, Wenyi Xie, P Lemaire, G Parsons, North Carolina State University**

Self-limiting atomic layer etching (ALE) is essential for enabling the manufacturing of complex transistor structures. Thermal ALE, based on thermal desorption of volatile etch products, is appealing for avoiding plasma-induced damages of sensitive device structures. However, thermal ALE process for metals is currently lacking. In our study, we demonstrated two thermal atomic layer etching processes based on the sequential oxidation-etch reaction schemes which allow controlled W to proceed for temperatures ≥ 275 and ≥ 200°C, respectively.

In the first part of our study, we investigated a thermal tungsten (W) ALE process using oxygen (O₂) and tungsten hexafluoride (WF₆). Based on insights gained from thermodynamic modeling, we proposed that W etching could proceed in two sequential reaction steps: 1) oxidation of tungsten, and 2) formation and removal of volatile WO₂F₂ during reaction with WF₆ (Supplemental, Figure 1a). Using in-situ Quartz Crystal Microbalance (QCM) analysis, we found the O₂ and WF₆ half reactions exhibit self-limiting characteristics therefore making the O₂/WF₆ process promising for W ALE. In addition, the etch rate is ~ 6.3 Å/cycle at 300°C but decreases to 0.34 Å/cycle when temperature decreases from 300°C to 220°C (Supplemental, Figure 1b). The significant decrease in etch rate is likely due to the limited volatility of WO₂F₂ at temperatures < 275°C as suggested by thermodynamic modeling results.

W etching with the O₂/WF₆ process is limited to temperatures ≥ 275°C, however lower temperature ALE processes are more desired for enabling selective deposition. Through further thermodynamic modeling studies, we find that a lower temperature W ALE process is viable when tungsten hexachloride (WCl₆) is used as the etchant instead of WF₆. Thermodynamic modeling results revealed that WCl₆ reaction with WO₃ can give rise to formation of volatile WO₂Cl₂ at temperatures ≥ 200°C (Supplemental, Figure 2a). Using in-situ QCM analysis, we found that W etching with O₂/WCl₆ process is self-limiting and proceeds readily for temperatures ≥ 220°C (Supplemental, Figure 2b).

In summary, we demonstrated thermally driven W ALE using O₂/WF₆ and O₂/WCl₆ processes, and our work on thermal W ALE serves to increase the fundamental understanding on ALE reactions and expand the base of available ALE processes for advanced material processing.

9:45am **ALE1-TuM-8 Modifying Thermal HF-based ALE Methods via Secondary Interactions with Alkali Compounds, John Hennessy, A Jewell, S Nikzad, Jet Propulsion Laboratory, California Institute of Technology**

Alternating exposure to trimethylaluminum (TMA) and hydrogen fluoride (HF) has been used previously in the ALD of AlF₃ thin films. At substrate temperatures higher than approximately 225°C, the same exposure can result in the thermal atomic layer etching (ALE) of thin films of Al₂O₃. In previous work, we have shown that TMA/HF exposure performed in the presence of lithium fluoride (LiF) can significantly increase the Al₂O₃ etch rate and reduce the transition temperature where etching dominates over deposition.[1] In this work, we expand this approach to study the effect of other alkali halide compounds such as NaCl, KBr, and CsI. These materials are introduced externally into our vacuum chamber and influence the process behavior over surprisingly large spatial scales. All materials are observed to have an enhancing effect on the ALE process with respect to the etch rate of Al₂O₃ at a given substrate temperature. In some cases these materials can enable the reduction of the substrate temperature where continuous etching of Al₂O₃ is observed to as low as 125°C, a regime where the deposition of AlF₃ would otherwise dominate the TMA/HF process. The choice of alkali material, choice of aluminum precursor, and process parameters like substrate temperature and precursor dose, can be exploited to tune the rate and selectivity of the thermal HF-based ALE process. We present characterization of these processes to etch Al₂O₃ in a self-limiting manner, and discuss applications of the method related to the performance improvement of aluminum optical components in the deep ultraviolet for space applications.

[1] J. Hennessy *et al.*, J. Vac. Sci. Technol. A 35, 041512 (2017).

Atomic Layer Etching

Room 104-106 - Session ALE2-TuM

Modeling of ALE

Moderators: Alok Ranjan, TEL Technology Center, America, LLC, Craig Huffman, Micron

10:45am **ALE2-TuM-12 The Role of Modelling in Understanding and Designing Processes for Thermal Atomic Layer Etch**, *Simon D. Elliott*, Schrödinger, Inc., Ireland; *S Natarajan*, Tyndall National Institute, Ireland
INVITED

Plasma-free (or so-called 'thermal') atomic layer etch (ALE) is often described as the inverse of atomic layer deposition (ALD). In this talk we discuss whether existing approaches for the atomic-scale modelling of ALD chemistries can also be applied to ALE, what new modelling approaches are being developed for ALE and what needs are still outstanding.

Examples of the successful ALE of oxides from the literature are classified into types according to their assumed mechanisms, focusing on continuous versus self-limiting reactions, on surface conversion versus ligand exchange reactions, and on redox steps. Corresponding thermodynamic and kinetic criteria are then proposed as a framework for the theoretical analysis and prediction of ALD processes. To examine the validity of this framework, energetics computed at the level of density functional theory (DFT) for the sample ALE reactions are presented and discussed. Many of the trends observed in experiment for the ALE of oxides like alumina and hafnia can thus be reproduced and understood with relatively little computational effort. The observed temperature dependence is broken down into entropy effects in individual ALE pulses. Moving beyond this simple framework, we discuss the most important reaction steps that need to be explicitly modelled for a full understanding of ALE. Early results are presented, including progress towards simulating the volatility of etch by-products. Comparisons are drawn with past work on ALD. A wish-list of future modelling needs is proposed.

11:15am **ALE2-TuM-14 Physical Damage Analysis of Atomic Layer Etching of Silicon using Molecular Dynamic Simulations**, *Ryoko Sugano*, *M Kurihara*, Hitachi R&D Group, Japan; *K Kuwahara*, Hitachi High-Technologies Corp., Japan; *S Hamaguchi*, Osaka University, Japan

As the device structures shrink to atomic dimensions, more precise etch processes are required with atomic-scale controllability and lower damage. Atomic layer etching (ALE) is considered to fulfill such requirements in the fabrication of next-generation 3D devices, rather than conventional reactive ion etching [1]. Anisotropic ALE can transfer the exact dimensions of mask patterns to the underlying layer. ALE is typically achieved by two sequential self-limiting surface reactions. For example, anisotropic silicon ALE (Si-ALE) was demonstrated by the use of cyclic repetitions of cryogenic adsorption of F atoms and the subsequent Ar ion irradiation [2]. Since then, various Si-ALE has been investigated with halogen gases for the Si surface modification and Ar ion bombardment for the removal of halogen-bonded Si atoms. Ar ion bombardment in a removal step, however, causes plasma induced damages even at energy below the sputtering threshold. Experiments with low-electron-temperature plasmas showed that surface damage was considerably mitigated when ion energy was less than -10 eV [3]. With an increase of the incident ion energy, both the etched depth and damage thickness increased. Hence, for a better control of anisotropic Si-ALE, the relationship between the etched depth and damage thickness must be clarified.

In this work, to obtain low-damage process conditions for anisotropic Si-ALE, we have used molecular dynamic (MD) simulations and examined the effects of adsorbed halogen species and ion energy. The Si-ALE process analyzed in this study is based on cyclic repetitions of Br or Cl adsorption and Ar ion bombardment steps. Interatomic potential functions used in the MD simulations are of Stillinger-Weber type [4]. Plasma induced damages were estimated by the structural change in the Si lattice of the underlying Si substrate. It has been found that both the damage and the halogen penetration-depths are larger in the case of Cl than in Br, presumably due to the atomic-size difference between Cl and Br. When Cl is used for adsorption, the number of desorbed SiCl_x is more than twice that of SiBr_x when Br is used under similar conditions. This is because the number of Si-Cl bonds in the damaged layer is much larger than that of Si-Br bonds. MD simulations have also shown that Si-ALE with Ar ion irradiation below 20 eV causes no damage in the underlying layer below 1 nm-depth from the surface in both cases of Br and Cl.

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

[2] Y. Horiike et al., J. Vac. Sci. Technol. A **8**, 1844 (1990).

[3] L. Dorf et al., J. Phys. D **50** 274003(2017).

[4] K. Miyake et al., Jpn. J. Appl. Phys. **53**, 03DD02 (2014).

11:30am **ALE2-TuM-15 Dimer Products from Ligand-Exchange Reactions During Thermal Atomic Layer Etching**, *Andrew Cavanagh*, *J Clancey*, *S Sharma*, *S George*, University of Colorado - Boulder

Thermal atomic layer etching (ALE) can be accomplished using sequential, self-limiting fluorination and ligand-exchange reactions. One example is Al_2O_3 ALE using sequential exposures of HF and $\text{Al}(\text{CH}_3)_3$. Fluorination by HF converts Al_2O_3 to AlF_3 . The ligand-exchange reactions are then believed to involve transmetalation where ligands are exchanged between the surface metal fluoride (AlF_3) and the gas phase metal precursor ($\text{Al}(\text{CH}_3)_3$). The products of these transmetalation reactions have been assumed to be monomeric metal species (e.g. $\text{AlF}(\text{CH}_3)_2$). In contrast, our recent quadrupole mass spectrometry (QMS) investigations have observed very little of the monomeric $\text{AlF}(\text{CH}_3)_2$ etch product. Instead, the main etch products are dimer species in form of $\text{AlF}(\text{CH}_3)_2$ - $\text{AlF}(\text{CH}_3)_2$ and $\text{AlF}(\text{CH}_3)_2$ - $\text{Al}(\text{CH}_3)_3$ (see supplemental Figure S1). These dimers are formed from the monomeric $\text{AlF}(\text{CH}_3)_2$ etch product with itself and with the $\text{Al}(\text{CH}_3)_3$ metal precursor.

To understand the relative stability between monomer and dimer reaction products, calculations were performed on all possible monomers and dimers that could be produced by the $\text{Al}(\text{CH}_3)_3/\text{AlF}_3$ ligand-exchange reaction. The potential energy surface for the reaction of $\text{Al}(\text{CH}_3)_3$ and AlF_3 confirms that dimers are the preferred etch product (see supplemental Figure S2). The dimers consist of a pair of bridging ligands between the Al metal centers and four terminal ligands. The bridging ligands can be (F, F), (F, CH_3) or (CH_3 , CH_3). The (F, F) bridges result in the most stable dimers while the (CH_3 , CH_3) dimers result in the least stable dimers. In agreement with the QMS results, these calculations predict that the $\text{AlF}(\text{CH}_3)_2$ - $\text{AlF}(\text{CH}_3)_2$ dimer with a (F,F) bridge and four terminal methyl groups is the most stable etch product.

The computational methodology has been applied to additional ligand-exchange reactions involving fluorinated Al_2O_3 , Ga_2O_3 and ZrO_2 substrates and various metal precursors including $\text{Al}(\text{CH}_3)_3$, $\text{Al}(\text{CH}_3)_2\text{Cl}$, SiCl_4 , GeCl_4 , SnCl_4 , and TiCl_4 . In all the systems, the calculations indicate that dimeric metal species are the most stable etch products. The ligand-exchange reactions occur, but the reaction products of the ligand-exchange remain associated in dimer metal species. The calculations predict that dimer metal species should be the stable, volatile etch products observed in future QMS studies.

11:45am **ALE2-TuM-16 Molecular Dynamics Simulation of SiO_2 Atomic-layer Etching (ALE) by Fluorocarbon and Argon Plasmas**, *Y Okada*, *M Isobe*, *T Ito*, *K Karahashi*, *Satoshi Hamaguchi*, Osaka University, Japan

As the sizes of modern semiconductor devices approach near-atomic scales, processing to create such devices in mass production scale also requires atomic-scale precisions. Recent technological advancement for atomic-scale processing includes the development of atomic-layer etching (ALE), where etching processes take place layer by layer with each step having self-limiting chemical reactions on the surface. In such a process, self-limiting reactions result in not only atomic-scale accuracy of processed structures but also process uniformity over a large area regardless of structure densities. In this study we have examined mechanisms of ALE processes of SiO_2 based on digital or pulsed application of fluorocarbon plasmas, using molecular dynamics (MD) simulations. In MD simulations, chemically reactive fluorocarbon radicals are first supplied to a SiO_2 surface with extremely low incident energy and a thin fluorocarbon layer is deposited there. Then the surface is irradiated with low-energy Ar^+ ions, which induces reactions between fluorocarbon and SiO_2 , typically forming volatile SiF_x and CO atoms, and the SiO_2 surface is etched until fluorocarbon on the substrate is essentially exhausted. In MD simulation, we have found that the actual reactions are not as simple as described above. In the Ar^+ ion irradiation step, preferential sputtering of O atoms occurs even at small ion incident energy, which makes the surface more Si rich and also promotes the formation of Si-C bonds in the presence of a deposited fluorocarbon layer. C atoms bonded with Si are hard to remove by low-energy Ar^+ ion irradiation and C tends to accumulate as fluorocarbon deposition steps are repeated, which may eventually lead to a complete etch stop and carbon deposition. On the other hand, a small amount of oxygen added to Ar^+ ion irradiation steps can contribute to more efficient removal of carbon from the surface and also supplement the loss of oxygen due to low-energy ion bombardment. The physical sputtering yield of SiO_x is lower when its oxygen content is closer to stoichiometric SiO_2 , so

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addition of a small amount of oxygen can also help self-limit the physical sputtering in the Ar⁺ ion irradiation step.

Atomic Layer Etching

Room 104-106 - Session ALE1-TuA

Applications for ALE

Moderators: Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, Harm Knoops, Eindhoven University of Technology

1:30pm **ALE1-TuA-1 Mechanism of HF Pulse in the Thermal Atomic Layer Etch of Al_2O_3** , *Suresh Kondati Natarajan*, Tyndall National Institute, Ireland; *S Elliott*, Schrödinger, Inc., Ireland

Alumina has excellent electrical insulation properties, which makes it an important material in the fabrication of semi-conductor devices. As the critical dimensions of such devices are decreasing rapidly, advanced material processing techniques with atomic precision have become necessary. Recently, a thermal atomic layer etch (ALE) process for alumina has been reported where HF and $Sn(acac)_2$ / tri-methyl aluminium (TMA) are used as precursors. Thermal ALE is different from conventional ALE in using thermally activated ligand exchange reactions for material removal instead of energetic ion bombardment or plasma. In the ALE of alumina, the HF pulse modifies alumina surface by forming a non-volatile AlF_3 layer and the subsequent $Sn(acac)_2$ / TMA exposure exchanges ligands with the surface resulting in the formation of volatile etch products.

In this talk, insights in to the mechanism of HF adsorption on alumina will be provided with the help of first principles calculations using density functional theory. On adsorption, a HF molecule dissociated spontaneously at the surface of alumina and formed surface bound Al-F and O-H species. At higher coverages, a hydrogen bonded network of dissociated and intact HF molecules was observed at the alumina surface. Partial dissociation of the adsorbed HF molecules was found to be energetically favorable than the dissociation of all adsorbed molecules. Energetic barriers ranging from +0.9 eV to +1.8 eV were found to be impeding the formation of water molecules. The desorption energy of water molecules were found to be ranging from +0.2 eV to +1.2 eV. Finally, based on the saturated coverage of dissociated F atoms (13.7 ± 0.3 F/nm²), the theoretical maximum of the etch rate was estimated to be -1.28 ± 0.03 Å/cycle.

1:45pm **ALE1-TuA-2 Low-K Dielectric Etch Challenges at the 7nm Logic Node and Beyond: Continuous-wave vs. Quasi-atomic Layer Plasma Etching Performance Review**, *Yen-Tien Lu*, Tokyo Electron

For logic nodes beyond 7nm, back-end-of-line (BEOL) patterning critical pitch is less than 40nm, which has direct impacts on low-K etch process window. As the pitch is reduced, RIE lag becomes more significant resulting in wider trenches having a faster etch rate compared to narrower trenches (Figure 1). Hence, the trench profile, via CD and height, and chamfer angle will vary in trenches depending on their width. Hard mask selectivity also becomes a concern for the dense trenches where the hard mask at smaller dimensions is more significantly affected by sputtering. Recently, the concept of atomic layer etching and quasi-atomic layer etch (Q-ALE) has been widely used in various applications for high selectivity requirements and ideal bottom trench profile engineering^{1,2}. However, little studying has been done on sub 40nm pitch BEOL dielectric etch with Q-ALE.

In this work, we investigate the impacts of Q-ALE on low-K materials compared to continuous wave (CW) plasma and pulsed plasma. We demonstrate that Q-ALE can be successfully used to suppress RIE lag in BEOL low-K materials at advanced pitches. In order to minimize low-K damage generated during the etching process, an inverse RIE lag process was also developed. These processes can be used with conventional etching processes to compensate RIE lag and result in optimum process performance (Figure 2). In addition, Q-ALE technique shows improved hard mask selectivity and results in lower pattern roughness. Finally, combining Q-ALE and CW processes can minimize wafer throughput impact from Q-ALE processes, which usually take significantly longer than CW processes (Figure 3).

References:

¹ S. D. Sherpa and A. Ranjan, *J. Vac. Sci. Technol. A*, **35**, 01A102, (2017)

² M. Wang, P. L. G. Ventzek, and A. Ranjan, *J. Vac. Sci. Technol. A*, **35**, 03130, (2017)

Keywords: RIE lag, quasi-ALE, pulsed plasma, low-K damage

2:00pm **ALE1-TuA-3 Precise Etching Profile Control by Atomic-scale Process**, *Yoshihide Kihara*, *T Katsunuma*, *M Tabata*, *T Hisamatsu*, *M Honda*, Tokyo Electron Miyagi Ltd., Japan **INVITED**

In recent years, with the progress of device miniaturization and increased challenges in the scale of integration as semiconductor devices, fine control of the surface reactions is required in the fabrication processes. In self-aligned contacts (SAC) process, ultra-high selectivity of SiO_2 etching towards SiN is required, for which we developed Quasi-ALE technique for SiO_2 etching. Quasi-ALE precisely controls the reaction layer thickness of the surface, by controlling the radical and ion flux independently. In Quasi-ALE, adsorption step contains radical supply onto the surface and activation step contains etching by ion bombardment. Quasi-ALE was able to improve the conventional trade-off between the etching ability on the micro slit portions and SiN selectivity in the SAC process [1].

We have advanced Quasi-ALE technology for control of etching profile. The advanced technology is called as rapid advanced cyclic etching (RACE) process. The RACE process is divided by process gas into several steps that have a different purpose as a function of each process gas. As a result, we can easily set optimum radical and ion fluxes and ion energy for each step. Therefore, RACE process enables even more precise control of the surface reactions.

TiN mask pattern is transferred to the underlying SiO_2 and low-k film in metal hard mask trench process of BEOL where TiN mask selectivity, chamfer profile control and critical dimension (CD) variation at wafer very edge are the big patterning challenges. In the conventional method, the process results show that there is a trade-off between TiN mask selectivity and chamfer profile. To address this issue, RACE process was adopted in BEOL trench process. With this method, we were able to control the chamfer profile while keeping a low TiN mask loss. This is because RACE process achieves very fine control of the surface reactions by maximizing the effect of each step in RACE process. In addition, RACE process was able to reduce the CD variation at wafer very edge. This is demonstrating that RACE process is effective technique for not only the etching performance but also the CD uniformity.

On the other hand, we developed new CD shrinking technique without CD loading that combines Atomic Layer Deposition (ALD) and etching [2]. To control etching profile precisely, ALD was adopted to various applications. In the presentation, we will introduce some etching performances.

1. M. Honda, T. Katsunuma, M. Tabata, A. Tsuji, T. Oishi, T. Hisamatsu, S. Ogawa and Y. Kihara, *J. Phys. D: Appl. Phys.* **50**, 234002 (2017)

2. M. Honda, "New Innovative Dielectric Etching Approaches by Controlling the Surface Reaction at Atomic-Level" 4th ALE 2017

Atomic Layer Etching

Room 104-106 - Session ALE2-TuA

Selective ALE

Moderators: Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, Harm Knoops, Eindhoven University of Technology

2:30pm **ALE2-TuA-5 Thermal Selective Etching on Metal Oxide and Nitride Film**, *Jinhyung Park*, Air Liquide Laboratories Korea, Republic of Korea

Highly selective etching of metal oxide, nitride and metal has been demonstrated by using metal fluoride. In addition, this etching was taking thermal dry etching without plasma assisted. Reports of thermal dry etching by using metal fluoride are very limited.¹ In this work we conducted etching test between 150 and 450oC on various metal oxides, nitrides and metal substrate. Some results showed selective etching that only desired film was etched and non-desired film was not etched under same conditions. Etching rate and selective tendency was also compared. Not only flat surface, it was confirmed that metal fluoride worked for dry etching of a film in patterned wafer.

Figure 1

Figure 1. SEM image of thermal etching of ZrO_2 deposited in patterned wafer

Figure 1 showed one example that etching of ZrO_2 in trench by using NbF_5 under different conditions. All etching results are analyzed by several methods such as ellipsometry, scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS). In this presentation, individual etching result of metal oxides (Nb_2O_5 , Ta_2O_5 , TiO_2 , ZrO_2 , HfO_2 , SiO_2 , Al_2O_3 , Y_2O_3), metal

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nitrides (TiN, TaN, SiN), metal (W) and their comparison will be shown and discussed.

[1] P. C. Lemaire, G. N. Parsons, Chem. Mat. 29, 6653(2017).

2:45pm **ALE2-TuA-6 Benefits of Atomic Layer Etching for Material Selectivity**, *Thorsten Lill, K Kanarik, S Tan, I Berry, V Vahedi, R Gottscho*, Lam Research Corp.

For most critical etch applications such as pattern-transfer and 3D structure formation, an essential requirement is material selectivity. By material selectivity we refer to etching one material (X) preferentially to another material (Y), where the extent of selectivity is commonly denoted by the ratio X:Y for the relative amounts etched. Etching has had to be selective since the earliest years and the development of selective processes has been developed at least over the last 40 years of plasma etching. In this talk, we will discuss the strategies of selective etching and how atomic layer etching (ALE) helps. Both directional and isotropic ALE schemes will be discussed, as well as the basic underlying strategies in both. The insights will be vital for exploiting ALE in the fabrication of future devices.

3:00pm **ALE2-TuA-7 Approaching Atomic Scale Precision for Etch Technology Needs in the Semiconductor Industry**, *Robert Bruce, J Papalia, M Sagianis, D Montalvan, H Miyazoe, N Marchack, S Engelmann*, IBM TJ Watson Research Center **INVITED**

As we advance beyond the 7nm technology node, the semiconductor industry has implemented ever more complex architecture for logic and memory devices. For example, stacked nanosheets are a potential successor to finFETs and the number of levels continue to rise in 3D-NAND memory. To enable manufacture of new 3D devices at this unprecedented level of scale and intricacy requires atomic precision in etching and patterning, both anisotropic and isotropic, with high selectivity of etching one material over a host of other materials. Atomic layer etching (ALE) is a concept with goal to achieve this atomic scale precision by separating the etch process into controlled, self-limited reactions.

Because a large part of integrated devices are composed of insulating materials such as SiO_x and SiN_x, it is essential to understand their fundamental etching behavior at the atomic scale. In this talk, the interaction of SiO_x and SiN_x in hydrofluorocarbon-based plasmas was investigated. Due to their differences in surface modification behavior, the etching process could be tuned so that SiO_x etches selectively to SiN_x, and vice versa. The etch process parameters that influence material selectivity were evaluated, and it was found that hydrogen content, ion energy and substrate temperature had significant impact to the etching behavior of SiN_x. The possibility of improving selectivity by separating deposition and etching in a quasi-ALE approach is also studied. These important observations provide essential guidance to a wide range of dielectric etch applications, such as self-aligned contact etching and spacer etching.

Nanostructure Synthesis and Fabrication

Room 104-106 - Session NS+ALE-TuA

Nanostructures II + ALE

Moderators: Robert Clark, TEL Technology Center, America, LLC, Yong Qin, Institute of Coal Chemistry, Chinese Academy of Sciences

4:00pm **NS+ALE-TuA-11 Atomic Layer Etching and Chemical Vapor Etching of 2D Materials and Metal Oxide Films using MoF₆-H₂O**, *Anil Mane, D Choudhury, S Letourneau, J Elam*, Argonne National Laboratory

To meet the milestones outlined in the semiconductor technology roadmap, precisely controlled layer-by-layer etching processes for metal oxides are required to enable the fabrication of 3D-semiconductor microelectronic devices. In addition, 2D-layered transition metal dichalcogenides (TMDs) with tunable electronic properties exhibit attractive material properties and are under intense investigation as alternatives to silicon. Therefore, integration of 2D-materials with compatible dielectric metal oxide growth as well as etching can pave the way to successful device fabrication. Moreover, both selective material growth and selective etching are required for the cost effective manufacturing of advanced microelectronics.

Here we have developed etching processes using alternating exposures to molybdenum hexafluoride (MoF₆) and H₂O vapor for ALD grown metal oxides and 2D-TMDs. The MoF₆-H₂O precursors offer several advantages including low cost, low processing temperature, and rapid and effective etching spanning the range from continuous etching to atomic layer etching (ALEt).

We have used in-situ quartz crystal microbalance (QCM) and Fourier-transform infrared spectroscopy (FTIR) measurements to monitor the deposition and etching of the metal oxides and 2D-TMDs layers. Next, the etched metal oxides and 2D-TMDs thin films were analyzed by spectroscopic ellipsometry to determine the thickness and refractive index, and the composition was determined by X-ray photoelectron spectroscopy (XPS). These ex-situ measurements confirmed the etching behavior findings from our in-situ studies. Here we will discuss the details of the MoF₆-H₂O based etching chemistry.

4:15pm **NS+ALE-TuA-12 Membranes by Atomic Layer Deposition: Design and Applications**, *Mikhael Bechelany*, Institut Européen des Membranes, France **INVITED**

Atomic layer deposition (ALD) is a thin film technology that in the past two decades rapidly developed from a niche technology to an established method. It proved to be a key technology for the synthesis of ultrathin film, the surface modification and the fabrication of complex nanostructured materials as well as the membrane tuning. [1]

In this work, we will give an overview about our activities on ALD, from the design of nanomaterials to membrane applications. After a short introduction to ALD, the versatility of the technique for the fabrication of novel nanolaminates thin films [2] and functional nanomaterials [3, 4] will be showed. Selected examples, focused on its use for the engineering of nanostructured functional materials and membranes targeting applications in energy (osmotic energy, biofuel cells and gas separation), environmental ((bio)-sensor and water purification) and health (DNA and proteins sensing) fields [5-9] will be discussed.

[1] **Advanced Materials**, 2012, 24, 1017

[2] **J. Phys. Chem. C**, 2016, 120, 5124–5132

[3] **Nano Energy** 1 (2012) 696

[4] **Nanoscale** 7 (2015) 5794

[5] **Journal of Materials Chemistry A**, 2016, 4, 6487-6494

[6] **Journal of Materials Chemistry A**, 2016,4, 17686-17693

[7] **Biosensors and Bioelectronics**, 2017, 92, 763–769

[8] **Journal of Materials Chemistry A**, 2014, 2 (48), 20650 – 20658

[9] **ACS Appl. Mater. Interfaces**, 2017, 9, 16669–16678

4:45pm **NS+ALE-TuA-14 Field-effect Transistor using Two-dimensional Electron Gas in ALD Al₂O₃/TiO₂ Ultrathin (<10 nm) Film Heterostructure Interface**, *Tae Jun Seok, Y Liu*, Hanyang University, Republic of Korea; *H Jung, S Kim*, Ajou University, Republic of Korea; *D Kim*, Hanyang University, Republic of Korea; *S Kim, J Jang*, Korea Basic Science Institute, Republic of Korea; *D Cho*, Chonbuk National University, Republic of Korea; *S Lee*, Ajou University, Republic of Korea; *T Park*, Hanyang University, Republic of Korea

Recently, two-dimensional electron gas (2DEG) has attracted great attention due to the observation of 2DEG at various heteroepitaxial perovskite oxide interfaces. Typically, epitaxial LaAlO₃/single-crystal SrTiO₃ (LAO/STO) heterostructure shows high density of electrons (~10¹³-10¹⁴ cm⁻²) confined at the oxide interface, where the density is about ~100 times higher than those of a typical semiconductor interface (~10¹¹-10¹² cm⁻²). Despite its high electrical performance, process schemes are not suitable for practical device applications because of their high cost in the production of the oxide single crystal and epitaxial layer. Although the formation of 2DEG using γ-Al₂O₃ and amorphous LAO with Al₂O₃ over-layers on STO substrate was demonstrated recently, single crystalline STO substrates are still required. Therefore, 2DEG at an oxide interface has not been realized *via* a mass-production compatible thin film deposition process, in contrast to 2DEG at the semiconductor interfaces.

In this work, we demonstrate a realization of 2DEG at the interface in an extremely thin film (< ~10 nm) heterostructure comprised of two binary oxide stacks of Al₂O₃/TiO₂ *via* atomic layer deposition (ALD) on a SiO₂/Si substrate without using an oxide single crystal or epitaxial substrate. The Al₂O₃/TiO₂ heterostructure was composed of a few nm-thick amorphous Al₂O₃ over-layer and poly-crystalline anatase-TiO₂ bottom layer. We achieved high electron density (~10¹³-10¹⁴ cm⁻²) and mobility (~4 cm²/V-s) in the 2DEG at the interface of ultrathin Al₂O₃/TiO₂ heterostructures, comparable to those obtained from epitaxial oxide heterostructures. More importantly, we demonstrate a new type of field-effect transistors (FETs) using Al₂O₃/TiO₂ heterostructures with a high on-current (I_{on}, > 12 A/m), high on/off current ratio (I_{on}/I_{off} > ~10⁸), low off current (I_{off}, ~10⁻⁸ A/m), and low sub-threshold swing (SS, ~100 mV/dec.), which outperforms the oxide

heterostructure-based FETs reported so far. Ultrathin ($< \sim 7$ nm) TiO_2 bottom layer in the proposed $\text{Al}_2\text{O}_3/\text{TiO}_2$ heterostructure prone to be fully depleted, allows an extremely low I_{off} , high $I_{\text{on}}/I_{\text{off}}$ ratio and low SS with maintaining high I_{on} via 2DEG channel with a high carrier density at the interface. The proposed new-type devices would provide a great opportunity for practical applications and mass-production of 2DEG devices, allowing a multi-level three-dimensional (3D) integration scheme. The detailed experimental results including new materials systems will be presented.

5:00pm NS+ALE-TuA-15 Increased WS_2 Crystal Grain Size by Controlling the Nucleation Behavior during Plasma Enhanced Atomic Layer Deposition, Benjamin Groven, A Nalin Mehta, KU Leuven, Belgium; H Bender, J Meersschaut, T Nuytten, T Conard, A Franquet, W Vandervorst, M Heyns, M Caymax, I Radu, A Delabie, IMEC, Belgium

Two-dimensional (2D) transition metal dichalcogenides such as molybdenum and tungsten disulfide (MoS_2 , WS_2) emerge as semi-conducting three-atom-thick layers that are widely applicable, for example as the complement of Si in ultra-scaled nanoelectronic devices at the back-end-of-line (BEOL) [1]. To exploit the potential of 2D layers in BEOL structures, they need to be grown using manufacturable deposition techniques in a highly crystalline structure with control over the orientation of the basal plane at low deposition temperatures ($< 450^\circ\text{C}$).

When grown by atomic layer deposition (ALD) for atomistic growth control and compatibility with temperature sensitive structures, the crystallinity and structure of 2D materials is determined by the nucleation mechanisms, which are currently not yet understood. In our earlier work, polycrystalline WS_2 with well-controlled composition (S/W ratio ~ 2) and 2D structure was grown by PEALD from WF_6 , H_2 plasma and H_2S on Al_2O_3 at 300°C [2]. The WS_2 layers suffered from a nanocrystalline grain structure (< 20 nm).

In this work, we show that the WS_2 crystal grain size can be increased from ~ 20 nm to beyond 200 nm by lowering the nucleation density. The latter is achieved by using a starting surface with a lower reactivity towards the PEALD precursors (i.e., thermally grown SiO_2), and by enhancing the mobility of the adsorbed species at higher deposition temperature ($< 450^\circ\text{C}$) and reactor pressure (Figure 1).

By analyzing the morphology of the WS_2 crystals, we derive a qualitative model for the nucleation behavior of WS_2 during the PEALD process. The SiO_2 starting surface is less reactive to the PEALD precursors compared to Al_2O_3 starting surfaces, which results in growth inhibition on SiO_2 . The PEALD precursors preferentially adsorb on the existing WS_2 nuclei. In combination with enhanced surface diffusion of the adsorbed species across both the SiO_2 starting surface as well as the growing WS_2 nuclei, lateral growth from WS_2 crystal edges is promoted which maximizes the WS_2 crystal grain size and develops a strong (0002) texture.

This work demonstrates how insight in the nucleation behavior of 2D materials can be used to increase the crystal grain size and control the basal plane orientation during ALD. A better understanding of these nucleation mechanisms is crucial to advance the field of ALD of 2D materials.

[1] 47th IEEE European Solid-State Device Research Conference (ESSDERC) 2017, pp. 212–215. T. Schram, et al.

[2] *Chem. Mater.* 2017, 29 (7), 2927–2938. B. Groven, et al.

5:15pm NS+ALE-TuA-16 Controlling Material Properties of Nanostructured WS_2 during Plasma ALD for Improved Electrochemical Performance, Shashank Balasubramanyam, L Wu, V Vandalon, M Verheijen, E Kessels, J Hofmann, A Bol, Eindhoven University of Technology, Netherlands

Transition metal dichalcogenides like WS_2 are promising candidates for sustainable production of H_2 through electrochemical hydrogen evolution reaction (HER), when engineered into nanostructures with exposed reactive edge sites. Controlling the various parameters during the plasma exposure step of plasma-enhanced ALD (PEALD) allows tailoring of material properties which can influence the HER performance. In this work, we demonstrate a novel approach to maximize the density of reactive edge sites in nanostructured WS_2 by tuning the composition of co-reactant gas mixture during the plasma exposure step of PEALD.

$\text{H}_2\text{S}+\text{Ar}$ and H_2 diluted $\text{H}_2\text{S}+\text{Ar}$ were used as co-reactant gas mixtures for tuning the plasma composition during PEALD of WS_2 . The addition of the strong reducing agent H_2 to the $\text{H}_2\text{S}+\text{Ar}$ plasma gas mixture can significantly influence the WS_2 growth behaviour and resulting material properties. The $\text{H}_2\text{S}+\text{Ar}$ plasma yielded a GPC of 0.8\AA while the $\text{H}_2\text{S}+\text{Ar}+\text{H}_2$ plasma increased GPC to 1.4\AA for the same metalorganic precursor bis(tertbutylimido)-

bis(dimethylamido)-tungsten, at a low temperature of 300°C . Transmission electron microscopy (TEM) studies revealed the growth of WS_2 ‘nanoflakes’ when using $\text{H}_2\text{S}+\text{Ar}$ plasma, while $\text{H}_2\text{S}+\text{Ar}+\text{H}_2$ plasma resulted in the growth of WS_2 ‘fins’. The nanoflakes comprised of closely packed basal planes with their edges predominantly terminating on the top surface, while the fins appeared to have higher surface area and were observed to taper out on the top surface. Rutherford backscattering spectroscopy studies indicated an excess S content for nanoflakes (S:W=2.2), while a S deficiency was observed for fins (S:W=1.9). In line with TEM studies, X-ray diffraction measurements showed differences in preferential orientation of crystals for nanoflakes and fins.

The HER performance of WS_2 nanoflakes was significantly better than of WS_2 fins. To reach a current density of $10\text{mA}/\text{cm}^2$, a relatively lower overpotential of $\sim 390\text{mV}$ was sufficient for the nanoflakes while a significantly higher overpotential of $\sim 460\text{mV}$ was required for the fins. In line with HER results, copper underpotential depositions on the respective nanostructures revealed a three-fold increase in the amount of reactive edge sites for nanoflakes when compared with fins. In order to further enhance the HER performance, catalytically superior WS_2 nanoflakes were grown on top of high surface-area WS_2 fins. This WS_2 stack yielded the best HER performance in our work (overpotential of $\sim 365\text{mV}$). To summarize, we demonstrate how PEALD can be used as a new approach to nanoengineer and enhance the HER performance of WS_2 by maximizing the density of reactive edge sites at low temperature.

Bold page numbers indicate presenter

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