Atomic Scale Processing Focus Topic
Room B130 - Session AP+PS+TF-ThM

Thermal Atomic Layer Etching

Moderators: Eric A. Joseph, IBM T.J. Watson Research Center, Harutyun Melikyan, Micron Technology

8:00am **AP+PS+TF-ThM1 A Challenge for Selective Atomic Layer Etching of Non-volatile Materials Using Organometalic Complex**, ***Yoshihide Yamaguchi***, *S. Fujisaki, K. Shinoda,* Hitachi, Japan; *H. Kobayashi, K. Kawamura, M. Izawa,* Hitachi High Technologies, Japan **INVITED**

Remarkable progress on atomic layer etching (ALE) for non-volatile materials has been made in recent years. The typical procedure for thermal ALE of non-volatile materials such as HfO_2 is cyclic repetitions of formation and desorption of the organometallic complex at a constant temperature [1]. The most significant problem in thermal ALE is formation of a volatile organometallic complex layer on the surface. The organometallic complex layer prevents diffusion of etching species into the deep at the formation step and must be easily removed at the desorption step. The thermal ALE of La_2O_3, however, is difficult to apply because the organo-lanthanum complexes are easily decomposed by mild heating (< 200 deg. C) and fail to prevent the diffusion. To solve this thermal instability, the authors have applied a thermal cycle ALE [2,3], which is a combination of a formation of the organo-lanthanum complex at a low temperature and a desorption of the complex at a high temperature. In this paper, several results of our challenge for thermal ALE of non-volatile materials using a selective organo-metallization reaction on the surface will be discussed. Some guiding principles for the organo-metallization reaction will also be explained.

A La_2O_3 thin-film sputtering deposited on a SiO_2/Si wafer was used as a sample. First, the La_2O_3 film was exposed to vapor mixture of a diketone and a stabilizer as the etchant gas at below 150 deg. C. Then the sample was annealed up to 250 deg. C. Temperature dependence in the procedure was also evaluated. After these consecutive processes, the sample was analyzed by scanning electron microscopy, X-ray photoelectron spectroscopy. Formation of the organo-lanthanum complex showed temperature dependent quasi-self-limiting characteristics. In the lower temperature range, the self-limiting characteristics enable precise control of the organo-lanthanum complex formation. In the higher temperature range, the continuous characteristics enable a higher etch amount per cycle with high selectivity. Several differences between chemistry with and without a stabilizer in the etching gas will be discussed. The high etching selectivity of La_2O_3 to HfO_2 was also demonstrated. From these findings, we conclude that practical ALE of La_2O_3 has been successfully demonstrated.

[1] Y. Lee et al., Journal of Vacuum Science & Technology A 36, 061504 (2018).

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

[3] Y. Yamaguchi et al., ALE workshop TuM4 (2018).

8:40am **AP+PS+TF-ThM3 Characterization of Isotropic Thermal ALE of Oxide Films and Nanometer-Size Structures**, ***Andreas Fischer***, *A. Routzahn, T.B. Lill,* Lam Research Corporation

In this work, we have characterized the reaction of aluminum oxide via the DMAC ligand exchange mechanism.

Fluorination studies of aluminum oxide were performed using NF_3, CF_4 or anhydrous HF, respectively. We also explored various methods of fluorination of the oxide surface such as thermal, in-situ or remote plasma, respectively, and found that a sufficient fluorine concentration could be obtained with either of the methods or reactants to enable atomic layer etching (ALE).

To understand reaction kinetics, we examined the interaction of aluminum fluoride (AlF_3) films with DMAC. We found that AlF_3 etched until it was completely consumed by DMAC. An analysis of its temperature-dependence allowed us to extract activation energies for the ligand exchange mechanism.

In a third part we demonstrated the utility of HF/DMAC reaction for isotropic ALE applied to nanometer-size metal oxide structures on wafers. Various metal oxides were etched and selectivities between oxides and potential mask materials were determined.

9:00am **AP+PS+TF-ThM4 Advanced Selective Chemical Dry Etch for Oxide and Si-based Material**, ***Li-Hung Chen***, *T. Kato, K. Nakahata, K. Takeya,* Tokyo Electron Technology Solutions Limited, Japan

As device features continuously shrink with introducing complex structures and new materials in semiconductor manufacturing, extremely high selectivity for etch processes have become more and more important. High selective chemical dry etch is developed utilizing a separated damage-free chemical removal chamber and sublimation chamber. The required selectivity is realized by using various chemistries and quantum mechanics analysis.

Firstly, HF/NH3 chemistry is used for oxide etch with high selectivity to SiN, Si, metals and resist. On the other hand, HF mono chemistry can etch SiN with high selectivity to oxide and Si. Quantum mechanics analysis revealed that NH_3 combined with HF enhances the SiO_2 reaction because of its lower activation energy. However, HF mono chemistry enhances the SiN reaction because of its lower activation energy than the oxide reaction[1)]. Secondly, Gas A chemistry is introduced for etching low quality oxide with selectivity >50 to both high quality oxide and SiN. The reaction rate barrier determined by quantum mechanics shows that etch reactivity with ALD-oxide is higher than with Th-SiO2 and SiN in Gas A etch process. Furthermore, Si and SiGe etch are evaluated with different Gas B/C ratio. Etch amount of Si is increased with increasing Gas C flow which can reduce activation energy from quantum mechanics simulation. Moreover, SiGe etching amount is decreased with increasing Gas C flow. This means that selectivity between Si and SiGe can be precisely controlled by Gas flow ratio.

Various applications can be realized by utilizing chemical dry etch with specific chemistries. For oxide etch processes such as fin recess, air gap, hard mask removal and surface clean, HF/NH3 chemistry can be used to meet critical criteria such as oxide selectivity to Si, SiN, resist and metal. CIP HW is developed to enhance throughput with excellent etch selectivity and uniformity. Additionally, HF mono-gas (or F-containing treatment) can dope Fluorine (F) into oxide film which is confirmed by depth profile analysis of secondary ion mass spectrometry (SIMS), and F implantation is known for dielectric breakdown life time improvement[2)]. Also, Gas A can be utilized in Silica oxide removal process, which requires high selectivity between low quality and high quality oxide. Finally, Si mandrel removal and Si or SiGe nanowire fabrication is introduced by controlling gas flow ratio. Further discussion will be presented on AVS 66th.

Reference

[1] T. Kato, et al., AVS 65th Int. Symp. & Exhibit. (2018)

[2] Y. Mitani, et al., Proc. Of IEEE P93-98 (1999)

9:20am **AP+PS+TF-ThM5 Mechanisms of Thermal Atomic Layer Etching (ALE) of Metal by Deprotonation and Complex Formation of Hexafluoroacetylacetone (hfacH)**, ***Abdulrahman Basher***[1], *I. Hamada,* Osaka University, Japan; *M. Krstic,* Karlsruhe Institute of Technology (KIT), Germany; *M. Isobe, T. Ito,* Osaka University, Japan; *K. Fink,* Karlsruhe Institute of Technology (KIT), Germany; *K. Karahashi, Y. Morikawa,* Osaka University, Japan; *W. Wenzel,* Karlsruhe Institute of Technology (KIT), Germany; *S. Hamaguchi,* Osaka University, Japan

Thermal atomic layer etching (ALE) may be used for precise and damageless etching of difficult-to-etch materials such as Ni, Co, NiFe, MgO, and CoFeB, which can be used as materials for magnetic tunnel junction (MTJ) stacks of magnetic random access memory (MRAM) devices. The goal of this study is to understand the mechanisms of surface chemical reactions during thermal ALE of metal in general with oxidation and exposure to organic molecules. As a model case, we consider a two-step thermal ALE process of nickel (Ni) with an oxidation step and a gas exposure step at an elevated substrate temperature [1]. In the latter step, hexafluoroacetylacetone (hfacH) $CF_3C(OH)=CHC(O)CF_3$ is used as a reactive gas. In the oxidation step, a thin layer of NiO is formed on the Ni film surface and, in the gas exposure step, only (part of) this NiO layer is removed and thus self-limiting etching of Ni is achieved. Our main question is why NiO is etched but Ni is not etched by hfacH. This mechanism is studied with first-principle simulation of interaction of hfacH with Ni and NiO surfaces.

First, we examined interaction of hfacH with a metallic Ni surface, using a simulation code STATE [2,3], which is based on density functional theory (DFT) with pseudo-potentials and a plane wave basis set. Computationally, a metal surface is better represented by a plane wave basis set in general.

[1] **Coburn & Winters Student Award Finalist**

It has been found in our simulation that, as an hfacH molecule approaches a metallic Ni surface with thermal velocity, it is more likely to be decompose and fragmented, rather than forming a hexafluoroacetylacetonate anion (hfac-) by deprotonation. This is consistent with earlier experimental observations [1,4]. The simulation clearly shows an energy threshold for deprotonation of hfacH with a metallic Ni surface.

Second, we examined interaction of enol hfacH with a NiO surface using a simulation code Turbomole [5], which is based on DFT but with Gaussian type orbitals. To better represent a NiO surface, we used the embedded cluster method (ECM) with Turbomole. It has been found that, as an hfacH molecule approaches a NiO surface, it is likely to deprotonate by transferring its hydrogen ion (H+) to an O atom of the NiO surface and the resulting hfac- tends to bond with a Ni atom of the surface because of the highly ionic nature of NiO, where Ni and O atoms are positively and negatively charged, respectively. In this way, volatile $Ni(hfac)_2$ and H_2O can be formed when hfacH molecules interact with a NiO surface. Reaction energies of such interactions have been evaluated from the simulations.

----

[1] T. Ito, et al., AVS 65th International Symposium & Exhibition (2018).

[2] Y. Morikawa, H. Ishii and K. Seki, Phys. Rev. B, **69**, 041403 (2004).

[3] I. Hamada, Physical Rev. B **89**, 121103 (2014).

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

[5] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. **162**, 165 (1989).

9:40am **AP+PS+TF-ThM6 Thermal Atomic Layer Etching of Amorphous and Crystalline Al_2O_3 Films**, ***Jessica A. Murdzek**, S.M. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) can be achieved with sequential, self-limiting surface reactions. One mechanism for thermal ALE is based on fluorination and ligand-exchange reactions. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming volatile products. Previous studies have demonstrated the thermal ALE of amorphous Al_2O_3 films. However, no previous investigations have explored the differences between the thermal ALE of amorphous and crystalline Al_2O_3 films.

This study explored the thermal ALE of amorphous and crystalline Al_2O_3 films. HF or XeF_2 was used as the fluorination reactant. Dimethylaluminum chloride (DMAC) or trimethylaluminum (TMA) was employed as the metal precursor for ligand-exchange. The amorphous Al_2O_3 films had a much higher etch rate per cycle than the crystalline Al_2O_3 films. When using HF and TMA at 300 °C, the amorphous Al_2O_3 was removed at 0.78 Å/cycle, whereas the crystalline Al_2O_3 showed no significant thickness removal after 250 cycles (See Supplemental Figure 1). When using XeF_2 and TMA at 300 °C, the etch rate was 0.66 Å/cycle for the amorphous Al_2O_3 film. In comparison, ALE only removed up to 10 Å of the crystalline Al_2O_3 film. XeF_2 may be able to fluorinate the near surface region of the crystalline Al_2O_3 film easier than the crystalline bulk of the film.

The differences between amorphous and crystalline Al_2O_3 are sufficient to obtain selective thermal ALE of amorphous Al_2O_3 in the presence of crystalline Al_2O_3. The investigations also examined the effect of annealing temperature on the etch rate per cycle. Amorphous Al_2O_3 was etched at approximately the same etch rate until the crystallization of amorphous Al_2O_3 at >880 °C. The thermal ALE of crystalline films is important because amorphous films may not crystallize easily when they are too thin. Consequently, amorphous films may have to be grown thicker, crystallized, and then etched back to obtain the desired ultrathin crystalline film thickness.

11:00am **AP+PS+TF-ThM10 Thermal Atomic Layer Etching (ALE) of Germanium-Rich SiGe Films**, ***Aziz Abdulagatov**, S.M. George,* University of Colorado at Boulder

The thermal atomic layer etching (ALE) of germanium-rich SiGe was demonstrated using an oxidation and "conversion-etch" mechanism (See Supplemental Figure 1). In this process, the SiGe surface was oxidized to a SiGe oxide layer using O_2. The SiGe oxide layer was then converted to an Al_2O_3 layer using trimethylaluminum (TMA). The Al_2O_3 layer was fluorinated by HF to an AlF_3 layer prior to the removal of the AlF_3 layer by ligand-exchange using TMA. The thermal ALE of SiGe films will be important for the fabrication of advanced MOSFET devices.

This study explored the thermal ALE of germanium-rich $Si_{0.2}Ge_{0.8}$ films. *In situ* spectroscopic ellipsometry was employed to monitor the thickness of both the $Si_{0.2}Ge_{0.8}$ and the surface oxide layer during ALE. These studies showed that the $Si_{0.2}Ge_{0.8}$ film thickness decreased linearly with number of reaction cycles while the surface oxide thickness remained constant. Using an O_2-HF-TMA reaction sequence, the $Si_{0.2}Ge_{0.8}$ ALE etch rate was 0.57 Å/cycle at 290°C. This etch rate was obtained using optimal reactant pressures of 25, 0.2 and 0.4 Torr, and dose times of 1.5, 1 and 1 s, for O_2, HF and TMA, respectively.

The $Si_{0.2}Ge_{0.8}$ ALE etch rate was lower at lower temperatures. Using an O_2-HF-TMA reaction sequence, the $Si_{0.2}Ge_{0.8}$ etch rate was reduced from 0.57 Å/cycle at 290°C to 0.07 Å/cycle at 225°C. The order of the reactant sequence also affected the $Si_{0.2}Ge_{0.8}$ etch rate. Changing the reactant sequence from O_2-HF-TMA to O_2-TMA-HF reduced the $Si_{0.2}Ge_{0.8}$ etch rate from 0.57 to 0.45 Å/cycle at 290°C. $Si_{0.2}Ge_{0.8}$ could also be etched selectively in the presence of Si and Si_3N_4. The $Si_{0.2}Ge_{0.8}$ etch rate was >10 times faster than the etch rate for Si or Si_3N_4 at 290°C (See Supplemental Figure 2).

11:20am **AP+PS+TF-ThM11 Thermal Atomic Layer Etching of GaN and Ga_2O_3 Using Sequential Fluorination and Ligand-Exchange Reactions**, ***Nicholas Johnson**, Y. Lee, S.M. George,* University of Colorado at Boulder

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

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

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

11:40am **AP+PS+TF-ThM12 Mechanistic Insights into Thermal Dry Atomic Layer Processing of Metals**, ***Andrew Teplyakov**,* University of Delaware **INVITED**

The mechanisms of thermally induced reactions of atomic layer deposition (ALD) and atomic layer etching (ALE) can be sometimes viewed as proceeding in opposite directions. However, for atomic layer processing of metals, that would mean that the best designed and most efficient reaction pathways leading to metal deposition would produce insurmountable energy barriers for a reverse process. If ligand detachment, exchange, and decomposition could be desirable for ALD, the etching of the same metals would require careful consideration of the etching mechanisms at the atomic and molecular level. Given that the mechanisms of ALE can be very complex, the key concepts and approaches will be described here for thermal dry etching processing, which would allow for eliminating the role of solvents and for distinguishing thermodynamic and kinetic regimes of etching. The mechanistic investigation of thermal dry etching of cobalt will be the primary target of this work. This process will be used to illustrate the limitations of the single-reagent etching by analyzing the reaction of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfacH) or 2,4-pentanedione (acetylacetone, acacH)) with a clean cobalt surface. Then the effects of surface oxidation and chlorination will be explored as a means of kinetically controlled process. Finally, a number of potential effects of the mechanisms of dry etching on the morphology of the surfaces produced and, specifically, on the "smoothing" effect of dry etching will be discussed.

Author Index

Bold page numbers indicate presenter

— A —
Abdulagatov, A.I.: AP+PS+TF-ThM10, **2**
— B —
Basher, A.H.: AP+PS+TF-ThM5, **1**
— C —
Chen, L.H.: AP+PS+TF-ThM4, **1**
— F —
Fink, K.: AP+PS+TF-ThM5, 1
Fischer, A.: AP+PS+TF-ThM3, **1**
Fujisaki, S.: AP+PS+TF-ThM1, 1
— G —
George, S.M.: AP+PS+TF-ThM10, 2; AP+PS+TF-ThM11, 2; AP+PS+TF-ThM6, 2
— H —
Hamada, I.: AP+PS+TF-ThM5, 1
Hamaguchi, S.: AP+PS+TF-ThM5, 1
— I —
Isobe, M.: AP+PS+TF-ThM5, 1
Ito, T.: AP+PS+TF-ThM5, 1
Izawa, M.: AP+PS+TF-ThM1, 1
— J —
Johnson, N.S.: AP+PS+TF-ThM11, **2**
— K —
Karahashi, K.: AP+PS+TF-ThM5, 1
Kato, T.: AP+PS+TF-ThM4, 1
Kawamura, K.: AP+PS+TF-ThM1, 1
Kobayashi, H.: AP+PS+TF-ThM1, 1
Krstic, M.: AP+PS+TF-ThM5, 1
— L —
Lee, Y.: AP+PS+TF-ThM11, 2
Lill, T.B.: AP+PS+TF-ThM3, 1
— M —
Morikawa, Y.: AP+PS+TF-ThM5, 1
Murdzek, J.A.: AP+PS+TF-ThM6, **2**
— N —
Nakahata, K.: AP+PS+TF-ThM4, 1
— R —
Routzahn, A.: AP+PS+TF-ThM3, 1
— S —
Shinoda, K.: AP+PS+TF-ThM1, 1
— T —
Takeya, K.: AP+PS+TF-ThM4, 1
Teplyakov, A.V.: AP+PS+TF-ThM12, **2**
— W —
Wenzel, W.: AP+PS+TF-ThM5, 1
— Y —
Yamaguchi, Y.: AP+PS+TF-ThM1, **1**