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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Author Index

Bold page numbers indicate presenter

— A —
Abdulagatov, A: ALE1-TuM-3, **1**
— B —
Blomberg, T: ALE1-TuM-6, 1
— C —
Cano, A: ALE1-TuM-5, **1**
Clancey, J: ALE1-TuM-5, 1
— E —
Elliot, S: ALE1-TuM-5, 1
— F —
Fujisaki, S: ALE1-TuM-8, **2**
— G —
George, S: ALE1-TuM-3, 1; ALE1-TuM-5, 1; ALE1-TuM-7, 2
Guo, X: ALE1-TuM-4, 1
— H —
Hamaguchi, S: ALE1-TuM-1, 1
Haukka, S: ALE1-TuM-6, 1
He, C: ALE1-TuM-4, 1
— I —
Ito, T: ALE1-TuM-1, **1**
— K —
Karahashi, K: ALE1-TuM-1, 1
Konh, M: ALE1-TuM-4, 1
— L —
Lin, X: ALE1-TuM-4, 1
— M —
Murdzek, J: ALE1-TuM-7, **2**
— N —
Natarajan, S: ALE1-TuM-5, 1
— O —
Opila, R: ALE1-TuM-4, 1
— P —
Pallem, V: ALE1-TuM-4, 1
— S —
Sharma, V: ALE1-TuM-6, **1**
— T —
Teplyakov, A: ALE1-TuM-4, **1**
Tuominen, M: ALE1-TuM-6, 1
— W —
Wang, Z: ALE1-TuM-4, 1
— Y —
Yuan, B: ALE1-TuM-4, 1