Monday Afternoon, June 29, 2020

Atomic Layer Etching
Room Baekeland - Session ALE2-MoA
ALE of Metal Oxides

Moderators: Venkateswara Pallem, AirLiquide, Ishii Yohei, Hitachi High Technologies

4:15pm **ALE2-MoA-12 Ab Initio Study on the Surface Reactions of Thermal Atomic Layer Etching of Al_2O_3*, Xiao Hu,*** Chemnitz University of Technology, Germany*; J Schuster, S Schulz,* Fraunhofer Institute for Electronic Nano Systems, Germany

Thermal ALE is a novel approach for the isotropic etching of materials with atomic-level precision [1]. This technology will be important for the fabrication of advanced semiconductor devices, such as GAAFET and 3D NAND-Flash. The goal of this work was to understand the chemical mechanisms of thermal ALE using ab initio calculations. We chose Al_2O_3 ALE using HF and $Al(CH_3)_3$ as the case study. In the first half-cycle of Al_2O_3 ALE, it has been known that the fluorine precursor HF reacts with the Al_2O_3 surface to form an intermediate AlF_3 layer and H_2O molecules [1, 2]. The present work specifically focused on the second half-cycle reaction, where the metal precursor $Al(CH_3)_3$ etches the intermediate AlF_3 layer releasing volatile by-products.

Ab initio thermodynamic calculations were performed to predict the preferred etch products. Several possible Al-monomers and -dimers have been considered as the gaseous products. The calculation results show that the Al-dimers are more stable than their corresponding monomers. The most favorable etch product is the $Al_2F_2(CH_3)_4$ dimer, where two F atoms bridge the adjacent Al centers.

The surface reactions between the AlF_3 surface and $Al(CH_3)_3$ were investigated using dispersion-corrected density functional theory (DFT-D). The etch of the pristine surface by $Al(CH_3)_3$ is unfavorable due to a large reaction barrier (> 3 eV). Stability of the AlF_3 surface can be reduced by surface modification where some surface F atoms are replaced by the CH_3 groups of $Al(CH_3)_3$. This step is accomplished by a ligand-exchange reaction, as shown in Fig.1. The transition state calculated by DFT agrees well with that proposed by George et al [1].

The subsequent etch of the modified surface proceeds via two possible pathways: (1) direct etching by $Al(CH_3)_3$ with formation of Al-dimers; and (2) desorption of etch products caused by surface reconstruction. In both cases, the etch kinetics is mainly determined by the number of surface CH_3 groups. The surface CH_3 has two positive roles in etch reactions. First, the strength of the $Al-CH_3$ bond is much weaker than that of the Al−F bond. Second, the F atom in AlF_3 has a coordination number of two, whereas the CH_3 group typically favors a coordination number of one. Therefore, some chemical bonds of AlF_3 have been broken after surface modification.

Lastly, based on a detailed understanding of the reaction mechanisms, we have discussed the strategies for the design and screening of reactive precursors for thermal ALE.

[1] George, S.M. and Lee, Y. ACS Nano, 2016, 10(5), 4889-4894. [2] Natarajan, S.K. and Elliott, S.D. Chem. Mater., 2018, 30(17), 5912-5922.

4:30pm **ALE2-MoA-13 Volatile Products from Thermal Atomic Layer Etching Observed using Mass Spectrometer with Line-of-Sight Detection*, Andrew Cavanagh,*** *A Lii-Rosales, S George,* University of Colorado - Boulder

Identification of gas products from thermal atomic layer etching (ALE) is critical to understand the underlying surface chemistry. Previous quadrupole mass spectrometry (QMS) experiments identified the etch products from Al_2O_3 ALE using HF and trimethylaluminum (TMA) as the reactants [1]. These experiments sampled gas products with no line-of-sight between the substrate surface and the QMS ionizer. These QMS experiments observed dimers of the etch product, dimethylaluminum fluoride (DMAF), with itself (DMAF + DMAF) or with TMA (DMAF + TMA) [1].

For higher sensitivity and no wall-effects, a new apparatus (Figure 1) was built to provide line-of-sight between the substrate and the QMS ionizer. In this apparatus, a small reactor containing a powder sample is positioned in a larger vacuum chamber. The etch products emerge from an aperture in the reactor and are supersonically expanded into a lower vacuum region. The etch products then pass through a skimmer into the even lower pressure region containing the QMS ionizer. With this arrangement, the reactor can be maintained at ~1 Torr. The etch products can also have line-of-sight to the QMS ionizer with the ionization region at ~10^{-8} Torr.

Using this new apparatus, the ligand-exchange reaction of DMAC with AlF_3 was examined to study thermal Al_2O_3 ALE using HF and DMAC as the reactants [2]. Various monomer and dimer species were observed versus temperature (Figure 2). DMAC dimers and DMAC dimers that have undergone Cl/F exchange with AlF_3 are detected at lower temperatures. The main etch product, $AlCl_2(CH_3)$, is observed with increasing intensity at higher temperatures >230 °C. The ligand-exchange reaction of $SiCl_4$ with ZrF_4 was also examined to study thermal ZrO_2 ALE using HF and $SiCl_4$ as the reactants [3]. SiF_xCl_y species are observed from the halogen ligand-exchange reaction at >240 °C (Figure 3). $ZrCl_4$ is observed as the main Zr-containing etch product at >240 °C. $ZrFCl_3$ is detected as an additional product at higher temperatures >320 °C.

[1] J.W. Clancey, A.S. Cavanagh, J.E.T. Smith, S. Sharma and S.M. George, “Volatile Etch Species Produced During Thermal Al_2O_3 Atomic Layer Etching”, *J. Phys. Chem. C* **124**, 287 (2020).

[2] Y. Lee and S.M. George, “Thermal Atomic Layer Etching of Al_2O_3, HfO_2, and ZrO_2 Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures”, *J. Phys. Chem. C***123**, 18455 (2019).

[3] Y. Lee, C. Huffman and S.M. George, “Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions”, *Chem. Mater.***28**, 7657 (2016).

5:00pm **ALE2-MoA-15 Blocking Thermal Atomic Layer Etching with Removable Etch Stop Layers*, David Zywotko,*** University of Colorado - Boulder*; O Zandi, J Faguet, P Abel,* TEL Technology Center, America, LLC*; S George,* University of Colorado - Boulder

Thermal atomic layer etching (ALE) can be performed using sequential fluorination and ligand-exchange reactions. For example, thermal Al_2O_3 ALE can be achieved using HF for fluorination and $Al(CH_3)_3$ (trimethylaluminum (TMA)) as the metal precursor for ligand-exchange [1]. Sequential exposures of HF and TMA lead to Al_2O_3 etch rates of 0.47 Å/cycle at 285°C. The ability to block thermal ALE selectively will be useful for advanced nanofabrication. This study demonstrates how thermal Al_2O_3 ALE can be blocked with removable ZrF_4 etch stop layers. In situ quartz crystal microbalance (QCM) measurements were utilized to monitor the etching and the effect of the etch stop layers.

The ZrF_4 etch stop layers could be deposited on Al_2O_3 using tetrakis(ethylmethylamido) zirconium and H_2O at 285°C. These reactants deposit ZrO_2 layers that are then converted to ZrF_4 during the subsequent HF exposure. Because $Al(CH_3)_3$ does not undergo ligand-exchange with ZrF_4 [2], the ZrF_4 layer serves as an etch stop layer. QCM measurements revealed that an initial ZrO_2 thickness of just one monolayer prior to fluorination was able to completely inhibit thermal Al_2O_3 ALE. Prior to reaching a ZrO_2 thickness of one monolayer, the etching inhibition was proportional to the ZrO_2 fractional coverage. The ZrF_4 etch stop layer was observed to arrest the thermal Al_2O_3 ALE for >100 ALE cycles.

The ZrF_4 etch stop layer could then be easily removed by a ligand-exchange reaction with $AlCl(CH_3)_2$ (dimethylaluminum chloride (DMAC)) [3]. The ZrF_4 etch stop layer could be applied and removed repeatedly without changing the Al_2O_3 etch rate. X-ray photoelectron spectroscopy (XPS) studies observed no trace of Zr on the Al_2O_3 surface after 7 cycles of DMAC and HF sequential exposures. Area selective deposition of the ZrF_4 etch stop would lead to area selective etching using HF and TMA as the reactants. Area selective deposition could be achieved based on selective reactant adsorption or substrate-dependent nucleation delays.

[1] Younghee Lee, Jaime W. DuMont and Steven M. George, “Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions”, *Chem. Mater.* **28**, 2994 (2016).

[2] Younghee Lee, Craig Huffman and Steven M. George, “Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions”, *Chem. Mater.***28**, 7657 (2016).

[3] Younghee Lee and Steven M. George, “ Thermal Atomic Layer Etching of Al_2O_3, HfO_2, and ZrO_2 Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures”, *J. Phys. Chem. C***123**, 18455 (2019).

5:15pm **ALE2-MoA-16 Mechanism of the HF Pulse in the Thermal Atomic Layer Etch of HfO_2 and ZrO_2: A First Principles Study***, Rita Mullins,* Tyndall National Institute, Ireland*; S Natarajan,* Aalto University, Finland*; S Elliott,* Schrödinger, Inc.*; M Nolan,* Tyndall National Institute, Ireland

HfO_2 and ZrO_2 are two high-k materials that are crucial in semiconductor devices. Atomic level control of material processing is required for fabrication of thin films of these materials at nanoscale device sizes. Thermal Atomic Layer Etch (ALE) of metal oxides, in which up to one monolayer of the material can be removed per cycle, can be achieved by sequential self-limiting fluorination and ligand-exchange reactions at elevated temperatures. However, to date a detailed atomistic understanding of the mechanism of thermal ALE of these technologically important oxides is lacking. In this contribution, we investigate the hydrogen fluoride pulse in the first step in the thermal ALE process of HfO_2 and ZrO_2 using first principles simulations. We also present a thermodynamic analysis approach to compare reaction models representing the self-limiting (SL) and continuous spontaneous etch (SE) processes taking place during an ALE pulse. Applying this to the first HF pulse on HfO_2 and ZrO_2 we find that thermodynamic barriers impeding continuous etch are present at ALE relevant temperatures. Explicit calculations of HF adsorption on the oxide surfaces allow us to investigate the mechanistic details of the HF pulse. A HF molecule adsorbs dissociatively on both oxides by forming metal-F and O-H bonds. HF coverages ranging from 1.0 ± 0.3 to 17.0 ± 0.3 HF/nm^2 are investigated and a mixture of molecularly and dissociatively adsorbed HF molecules is present at higher coverages. Theoretical etch rates of -0.61 ± 0.02 Å /cycle for HfO_2 and -0.57 ± 0.02 Å /cycle ZrO_2 were calculated using maximum coverages of 7.0 ± 0.3 and 6.5 ± 0.3 M-F bonds/nm^2 respectively (M = Hf, Zr).

5:30pm **ALE2-MoA-17 Thermal Atomic Layer Etching of Ta_2O_5 and TaN using BCl_3 and HF: Evidence for a Conversion-Etch Mechanism***, N Johnson,* ***Steven M. George,*** University of Colorado - Boulder

Ta_2O_5 ALE was demonstrated using BCl_3 and HF as the reactants. The Ta_2O_5 ALE surface chemistry could proceed via a fluorination and ligand-exchange mechanism or a conversion-etch mechanism. The experimental results support a conversion-etch mechanism. BCl_3 is believed to convert the surface of Ta_2O_5 to a B_2O_3 surface layer via the favorable conversion reaction $Ta_2O_5 + 10/3\ BCl_3(g) \rightarrow 5/3\ B_2O_3 + 2TaCl_5(g)$ [$\Delta G°(250°C = -38$ kcal]. HF can then spontaneously etch the B_2O_3 surface layer via the favorable reaction $B_2O_3 + 6HF(g) \rightarrow 2BF_3(g) + 3H_2O(g)$ [$\Delta G°(250°C = -17$ kcal] [1]. In contrast, HF fluorination of Ta_2O_5 to TaF_5 or $TaOF_3$ is thermochemically unfavorable.

In situ spectroscopic ellipsometry and *ex situ* x-ray reflectivity measurements were employed to study Ta_2O_5 ALE. Evidence for the conversion of Ta_2O_5 to B_2O_3 was provided by the dependence of the Ta_2O_5 etch rate on BCl_3 exposure and BCl_3 pressure. The Ta_2O_5 etch rate increased progressively with both longer BCl_3 exposures and higher BCl_3 pressures. The longer BCl_3 exposures and higher BCl_3 pressures convert more Ta_2O_5 to B_2O_3. Using three BCl_3 exposures (130 mTorr for 30 s) and one HF exposure, the Ta_2O_5 etch rate was 1.05 Å/cycle at 250°C (Figure 1). Under these conditions, the Ta_2O_5 etch rates increased with temperature ranging from 0.36 Å/cycle at 200°C to 1.96 Å/cycle at 295°C. Ta_2O_5 etch rates also increased at higher BCl_3 pressure. The etch rates varied from 0.48 to 1.46 Å/cycle using one BCl_3 exposure (30 s) at BCl_3 pressures from 130 to 1000 mTorr, respectively (Figure 2).

TaN ALE was also demonstrated using an O_3 oxidation step to oxidize TaN to Ta_2O_5. The Ta_2O_5 was then etched using BCl_3 and HF as the reactants. TaN ALE was performed using supercycles defined by an O_3 exposure followed by 60 Ta_2O_5 ALE cycles using BCl_3 and HF as the reactants. The etch rate was 38 Å/supercycle at 250°C (Figure 3). This high TaN etch rate was attributed to the large Ta_2O_5 thickness produced by O_3 oxidation. The oxidation of TaN using O_3 was studied using x-ray reflectivity measurements. TaN oxidation was observed to be fairly self-limiting at Ta_2O_5 thicknesses of 60-70 Å after longer O_3 exposures at 250°C.

[1] N.R. Johnson and S.M. George, "WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Mechanisms" *ACS Appl. Mater. Interfaces***9**, 34435 (2017).

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