Atomic Layer Etching
Room Hall 3F - Session ALE2-TuM

Thermal Gas-phase ALE

Moderators: Prof. Dr. Heeyeop Chae, Sungkyunkwan University (SKKU), Jean-François de Marneffe, IMEC

10:45am **ALE2-TuM-12 Thermal Etching of Metals and Metallic Materials for Gate-All-Around Devices***, **Dimitri Kioussis**, S. Karumuri, M. Uddin, S. Barnhill, Y. Huang, B. Erickson,* Intel Corporation **INVITED**

Isotropic Vapor Etch and Atomic Layer Etching (ALE) with extreme high selectivity have become essential technologies to continue Moore's law cadence for fabrication of next generation logic transistors beyond 2nm node. This talk reviews the status of Vapor Etch and ALE processes at Intel for etching various materials such as metals, metal nitrides, and metal oxides used across various sections of the process flow. The talk will outline basic thermodynamic principles and reaction kinetics as they apply to these reactions. Will discuss why in the nonsaturation mode etch anisotropies may occur that can lead to unwanted performance variations in high aspect ratio devices due to topological constraints imposed on the delivery of reactants and removal of reactant by-products. While ALE involves sequential modification of the etch surface followed by ligand exchange to etch the material, thermal pseudo-ALE (Tp-ALE) uses thermal activation, instead of surface modification. Thereby, ligand exchange reacts with metal/metallic surfaces with or without surface modification. These two unique approaches offer atomic layer precision in removing metals/metallic films selective to other materials in the stack. This talk will briefly demonstrate the capability of ALE, Tp-ALE as well as combination approach in etch back, recess, and complete removal applications.

11:15am **ALE2-TuM-14 Low Temperature, Conversion-Free Thermal Atomic Layer Etching of Zinc Oxide using Hydrofluoric Acid and Trimethylgallium***, **Taewook Nam**, D. Zywotko, J. Partridge, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) processes have been developed based on various etching mechanisms. For example, metal oxides such as Al_2O_3, HfO_2, and ZrO_2 are etched based on "fluorination–ligand exchange" reactions. ALE studies have also shown that materials can be converted to a different material by reaction with the ALE precursors. The "conversion" based etching mechanism has been confirmed for ZnO ALE using hydrofluoric acid (HF) and trimethylaluminum (TMA). This study introduces a conversion-free thermal ZnO ALE using HF and trimethylgallium (TMG). ZnO thermal ALE using HF and TMG was studied using a variety of techniques including quartz crystal microbalance (QCM) and quadruple mass spectrometry (QMS). ZnO films were first deposited using atomic layer deposition (ALD) using diethylzinc (DEZ) and water (H_2O) at 100 °C. QCM measurements during ZnO ALE then observed digital mass gains during HF exposures and pronounced mass losses during TMG exposures. Under saturation conditions, the etch rates were 0.24, 0.52, 0.97, 1.35, 1.92, and 3.82 Å/cycle at 30, 60, 100, 150, 200, and 300 °C, respectively. One notable difference between ZnO ALE using HF/TMA or HF/TMG is that the etching can be achieved at 30 °C using HF/TMG, whereas ZnO ALE using HF/TMA requires temperatures ≥ 240 °C. To understand the temperature differences between the two chemistries, TMA and TMG were individually exposed to fresh ZnO ALD films. The mass after TMA exposure showed a pronounced decrease because of the conversion reaction. The TMA exposure converts ZnO to Al_2O_3. HF can then adsorb on the fluorinated Al_2O_3 surface. Subsequently, this HF can react with TMA to produce AlF_3 ALD at temperature < 240 °C. In contrast, the mass increased after TMG exposure on fresh ZnO ALD films because of TMG adsorption on the ZnO surface. HF then fluorinates ZnO to ZnF_2 and HF does not strongly adsorb on the ZnF_2 surface. Consequently, TMG does not react with HF to produce GaF_3 ALD. Because GaF_3 ALD does not compete with ZnO ALE, ZnO ALE can be performed at extremely low temperatures down to 30°C. QMS experiments were also performed to identify etch products during ZnO ALE using HF and TMG. The QMS experiments support the "fluorination-ligand exchange" reactions without conversion during ZnO ALE using HF/TMG.

11:30am **ALE2-TuM-15 Thermal Atomic Layer Etching of the Indium Gallium Zinc Oxide (IGZO) Family by Fluorination and Ligand-Substitution Hydrogen-Transfer Reactions***, **Troy Colleran**, J. Partridge, A. Abdulagatov, S. George,* University of Colorado at Boulder

Indium Gallium Zinc Oxide (IGZO) and its component metal oxides are important oxide semiconductors. Etching these metal oxides will be needed to fabricate thin channels for transistors. The thermal ALE of In_2O_3, Ga_2O_3, ZnO, and IGZO was achieved using sequential fluorination and ligand-substitution hydrogen-transfer (LSHT) reactions at 200°C. The two-step etching process was performed by first fluorinating the metal oxide using HF. Following fluorination, volatile release of the metal fluoride was accomplished using acetylacetone (Hacac). LSHT with Hacac leads to volatilization of the metals as stable, metal acetylacetonate compounds ($M(acac)_x$; M = In, Ga, Zn). During the LSHT reaction, acac from Hacac substitutes for fluorine in the metal fluoride. Hydrogen from Hacac also transfers to the metal fluoride to form HF. Etching of IGZO films was measured by *in situ* spectroscopic ellipsometry studies. IGZO etch rates of 0.3, 0.4 and 0.6 Å/cycle were measured at 200, 230 and 250°C, respectively, on IGZO thin films. Quadrupole mass spectrometry (QMS) studies also measured the etching of In_2O_3, Ga_2O_3 and ZnO powders at 200°C. In_2O_3 and Ga_2O_3 ALE were confirmed by the evolution of $In(acac)_3$ and $Ga(acac)_3$, as well as HF, during Hacac exposures after fluorination of the respective metal oxide. ZnO was found to be spontaneously etched by Hacac as evidenced by the continuous evolution of $Zn(acac)_2$ and H_2O during Hacac exposure despite no previous fluorination. Time-dependent studies of the etch products were also performed using QMS. The evolution of $M(acac)_x$ and HF during Hacac exposures on a previously fluorinated metal oxide was consistent with the proposed etch mechanism. The decay in $M(acac)_x$ signal intensity during Hacac exposures was evidence of self-limiting LSHT reactions. The spontaneous etching of ZnO using Hacac exposures did not prevent the thermal ALE of IGZO films.

11:45am **ALE2-TuM-16 Designing an ALE Process and Uncovering the Etching Mechanism for a 2D van Der Waals Material: Ternary Transition Metal Chalcogenide $CrPS_4$***, **Marissa Pina**, M. Whalen, J. Xiao, A. Teplyakov,* University of Delaware

$CrPS_4$ is a 2D van der Waals material in the ternary transition metal chalcogenide (TTMC) class of compounds. $CrPS_4$ is a semiconductor with A-type antiferromagnetic ordering, so thin flakes a few layers thick can display ferromagnetic or antiferromagnetic behavior depending on whether there is an odd or even number of layers.

In order to understand the magnetism down to the monolayer limit and their dynamic excitations in magnons and excitons, and make devices based on 2D magnetic materials viable for industry, 2D materials with well-controlled layer structures have to be produced. The existing methods for controlling $CrPS_4$ thickness, such as mechanical and liquid exfoliation, are either not well controlled or introduce damage to the crystal structure. In this study, we will show that thermal atomic layer etching (ALE) can be used to controllably etch the 2D crystals of this material without contaminating them. Ultimately, using ALE to manipulate the thicknesses of these flakes will allow for controlling their magnetic and dynamic optical properties.

$CrPS_4$ flakes were exfoliated onto a gold film from a single crystal via mechanical exfoliation. Thermal ALE cycles were performed in an ultra-high vacuum chamber. Each cycle consisted of a chlorine dose at elevated temperature using a solid-state electrochemical chlorine source, followed by an acetylacetone dose at elevated temperature. Atomic force microscopy was used to determine an average etching rate of 0.10 ± 0.07 nm/cycle. Although the etching rate appeared to depend on the thickness of the flakes, this average removal rate was recorded for 75 different points for flakes ranging from several nanometers to 90 nm in thickness. ALE also removed the island defects caused by exfoliation from the top of the flakes. XPS and ToF-SIMS were used to follow chemical changes in the material and to interrogate the distribution of etchant components within the flakes. The formation of chemical species containing acetylacetonate ligands was confirmed for all the components (Cr, P, S) of this TTMC, and the chlorination was followed in ToF-SIMS depth-profiling experiments. The ALE process that resulted in controlled material removal did not result in measurable surface contamination. Importantly, the etching of $CrPS_4$ is highly temperature-dependent, as lowering the process temperature by even 30 °C does not result in noticeable etching.

Author Index

Bold page numbers indicate presenter

— A —
Abdulagatov, A.: ALE2-TuM-15, 1
— B —
Barnhill, S.: ALE2-TuM-12, 1
— C —
Colleran, T.: ALE2-TuM-15, **1**
— E —
Erickson, B.: ALE2-TuM-12, 1
— G —
George, S.: ALE2-TuM-14, 1; ALE2-TuM-15, 1
— H —
Huang, Y.: ALE2-TuM-12, 1
— K —
Karumuri, S.: ALE2-TuM-12, 1
Kioussis, D.: ALE2-TuM-12, **1**
— N —
Nam, T.: ALE2-TuM-14, **1**
— P —
Partridge, J.: ALE2-TuM-14, 1; ALE2-TuM-15, 1
Pina, M.: ALE2-TuM-16, **1**
— T —
Teplyakov, A.: ALE2-TuM-16, 1
— U —
Uddin, M.: ALE2-TuM-12, 1
— W —
Whalen, M.: ALE2-TuM-16, 1
— X —
Xiao, J.: ALE2-TuM-16, 1
— Z —
Zywotko, D.: ALE2-TuM-14, 1