Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE2-TuM

Thermal and Gas-Phase ALE

Moderators: Anil Mane, Argonne National Laboratory, **Fred Roozeboom**, University of Twente

10:45am **ALE2-TuM-12 In Situ ALE/ALD Surface Engineering for Reduced Dielectric Loss in Superconducting Quantum Circuits**, ***Neha Mahuli***, Amazon **INVITED**

Coherence in superconducting quantum circuits is predominantly limited by loss from imperfect surfaces and interfaces, yet atomic layer deposition (ALD) and atomic layer etching (ALE) remain relatively unexplored. In this talk, we present ALD and ALE as a surface-engineering platform for superconducting quantum devices, highlighting performance gains and future opportunities. We describe a post-fabrication, in situ surface treatment integrating ALE and ALD to reduce dielectric loss in aluminum (Al)–based coplanar waveguide (CPW) resonators and transmon qubits on silicon substrates. The process involves conformal removal of native aluminum oxide using thermal ALE at 300°C (trimethylaluminum (TMA) and Hydrogen fluoride(HF)–pyridine chemistry), followed by controlled regrowth of a thin Al2O3 layer using ALD at the same temperature. Surface characterization indicates reduced organic contamination, formation of a thinner Al-rich oxide, and effective cleaning of patterned structures, including metal sidewalls. Applying this treatment to CPW resonators reduces two-level system (TLS) loss at single-photon power by a factor of two. Similarly, for Al transmon qubits, the combined ALE+ALD process increases the mean quality factor by a similar factor, with select devices exceeding 9 x 10^6 million and energy relaxation times above 0.4 ms. Finally, we outline ongoing efforts and some initial results to disentangle the roles of etching and encapsulation, including different ALE chemistries (thermal vs plasma), and in situ ALD of alternative low-loss dielectric capping layers, underscoring the potential of ALD/ALE for surface control in superconducting quantum hardware.

11:15am **ALE2-TuM-14 Fluorine-Free Thermal Atomic Layer Etching of ZrO_2 Using $H_2O/SOCl_2$ Chemistry for Damage-Free Etch-Back of High-k Dielectrics**, ***Gyeong Min Jeong***, *Jihoon Shin, Jin-Seong Park,* Hanyang University, Republic of Korea

As semiconductor devices continue to scale down, precise dimensional control of individual device components has become increasingly critical. In this context, atomic-scale processing techniques have emerged as key enablers for next-generation semiconductor manufacturing. Among them, thermal atomic layer etching (ALE) has attracted attention as a surface-reaction-driven process capable of removing materials with atomic-layer precision through sequential surface modification and material removal steps. Compared to conventional plasma-based etching, thermal ALE minimizes sputtering-induced damage and effectively suppresses surface roughening. High-k dielectric materials are widely employed as replacements for Si-based insulators in advanced semiconductor devices, enabling sufficient capacitance retention even at deeply scaled technology nodes. However, the dielectric properties of high-k oxides are strongly correlated with their crystalline phases, and achieving ultrathin crystalline films with well-controlled thickness remains challenging. An etch-back approach, in which sufficiently thick crystalline films are first deposited and subsequently thinned while preserving crystallinity, is therefore required. Thermal ALE is well suited for this purpose due to its inherently low-damage characteristics. Most reported thermal ALE processes for high-k materials normally use fluorine-based sources. From this point of view, we propose a novel thermal ALE process for zirconium dioxide (ZrO_2) that does not use the fluorination agent. ZrO_2 films were etched using alternating exposures of H_2O (water) and $SOCl_2$ (thionyl chloride), achieving a self-limiting etch rate of approximately 0.07 Å per cycle. chlorine residues were not detected within the ZrO_2 layer after etching. Surface hydroxylation induced by H_2O exposure forms a reactive termination that facilitates subsequent reactions with $SOCl_2$, enabling continuous and controlled etching. The proposed reaction mechanism is further supported by density functional theory (DFT) calculations. This fluorine-free thermal ALE approach provides precise, damage-free thickness control while preserving the crystalline properties of high-k dielectrics, offering a promising alternative to conventional fluorine-based etching processes for advanced semiconductor manufacturing.

11:30am **ALE2-TuM-15 Thermal Atomic Layer Etching by Halogenation and Ligand-Addition Using N-Heterocyclic Carbenes**, ***Aziz Abdulagatov***, University of Colorado Boulder; *Charles Dezelah, Matthew Surman,* ASM Microchemistry Ltd., Finland; *Steven George,* University of Colorado Boulder

N-heterocyclic carbenes (NHCs) are strong electron pair donors and can bind to metal centers by ligand-addition.In this study, etching of Al_2O_3 was demonstrated using halogenation with hydrofluoric acid (HF) followed by ligand-addition using NHCs.The NHC sources were 1,3-dimethylimidazolium-2-carboxylate ($IMeCO_2$) or 1,3-di-tert-butylimidazol-2-ylidene (ItBu) (**Figure 1**).The thermal ALE of Au and Co was also demonstrated using hydrochloric acid (HCl) together with $IMeCO_2$ or ItBu.The studies were conducted using in situ quartz crystal microbalance (QCM) measurements.

Al_2O_3 thermal ALE was achieved using sequential HF and $IMeCO_2$ or ItBu exposures at temperatures from 230 to 290 °C.QCM profiles showed a self-limiting mass gain during fluorination and a self-limiting mass loss during the NHC ligand-addition step (**Figure 2a**).The mass change per cycle yielded an etch rate of 3.3 Å per cycle at 290 °C. The spontaneous etching of Al_2O_3 films was also observed during exposure to 2,2-difluoro-1,3-dimethylimidazolidine (DFI) (**Figure 1**).DFI provides both fluorination and ligand-addition by the NHC remaining after fluorination.DFI leads to continuous Al_2O_3 spontaneous etching at 200 to 270 °C.

The NHCs were also effective for Au and Co thermal ALE.Sequential exposures of HCl and $IMeCO_2$ or ItBu led to a linear mass decrease with the number of ALE cycles. The maximum Au mass change yielded an etch rate of 0.83 Å per cycle at 250 °C using HCl and $IMeCO_2$ (**Figure 2b**). For Co, the maximum etch rate was 3.0 Å per cycle at 290 °C using HCl and ItBu. These ALE processes are believed to proceed through the formation of volatile metal chloride–carbene adducts.The cycle times during Au and Co ALE were much shorter than earlier cycle times for Au and Co ALE measured using phosphines for ligand-addition.

11:45am **ALE2-TuM-16 Influence of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of MoS_2**, ***Spencer P. Smith***, *Jacob A. Tenorio, Icelene Leong, John D. Hues, Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has proven to be a transformative technique for atomic scale processing of two-dimensional (2D) materials, including molybdenum disulfide (MoS_2), a promising material in the semiconductor industry because of its high mobility in its monolayer form. Precise etching of MoS_2 films can offer a route to desired electrical and optical properties through controlling film thickness. Previous research reported MoF_6 and H_2O as precursors for thermal ALE of MoS_2. Here, we report on progress with alternative fluorination and oxygenation sources and assess their effectiveness of thermal ALE of MoS_2. Oxygen sources include H_2O and O_3, and fluorine sources include HF/Pyridine and MoF_6. Etch rates, uniformity, and surface chemistry following ALE were characterized through spectroscopic ellipsometry, atomic force microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The results of ALE of amorphous MoS_2 with HF indicated that there were no signs of etching with H_2O at 200 °C or 300 °C. ALE with HF and O_3 produced a mass loss per cycle of 25 ng/cm^2 at 200 °C and an etch per cycle (EPC) of 0.4 Å, similar to prior results of 0.5 Å/cyc with MoF_6 and H_2O. However, MoF_6 with O_3 at 200 °C on amorphous MoS_2 films exhibited non-self-limiting etch behavior with a mass loss per cycle of 126 ng/cm^2. Lowering the temperature to 150 °C resulted in self-limiting ALE with a mass loss per cycle of 63 ng/cm^2. Although surface oxygen concentrations increased from etching, surface morphology showed little change on amorphous films. Results for application of these chemistries to crystalline MoS_2 films will be discussed. This research further broadens the capabilities of atomic layer etching for precise processing of 2D materials.

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