

## Atomic Layer Etching

### Room Tampa Bay Salons 3-4 - Session ALE1-TuM

#### Wet ALE and ALE Modeling

**Moderators:** Jeffrey W. Elam, Argonne National Laboratory, Geun Young Yeom, Sungkyunkwan University

8:00am **ALE1-TuM-1 A Dry-Wet Quasi-ALE Approach for Transition Metals: Tungsten as a Model System**, *Cinzia Chan*, KU Leuven and Imec, Italy; *Jean-Francois de Marneffe*, IMEC Belgium; *Christopher Gort*, TU Darmstadt, Germany; *Jill Serron*, IMEC Belgium; *Marta Agati*, IMEC Belgium, Italy; *Felix Seidel*, IMEC Belgium; *Jan P. Hofmann*, TU Darmstadt, Germany; *Stefan De Gendt*, KU Leuven and Imec, Belgium; *Dennis H. van Dorp*, IMEC Belgium, Netherlands

**INVITED**

We demonstrate a hybrid dry-wet quasi-atomic layer etching (Q-ALE) process using tungsten as a model case, combining a self-limiting O<sub>2</sub> plasma oxidation (modification) step with a wet-chemical oxide removal step in 1 M HCl. In the study of the modification step, O<sub>2</sub> plasma oxidation was selected for its self-limiting behavior and benchmarked against wet oxidation, which instead produces highly soluble oxides in aqueous solution. The removal step was quantified by ICP-MS, revealing an initially high etch rate that decreases and stabilizes to a background value. This behavior is attributed to the rapid dissolution of plasma-generated bulk WO<sub>3</sub>, followed by progressively slower removal as the interface approaches a suboxide-rich layer, and finally a steady-state regime governed by continuous re-oxidation and metal dissolution. Although the background etch rate is very slow (0.03 Å·min<sup>-1</sup>), in Q-ALE operation the removal step is intentionally stopped before reaching this background regime, enabling controlled and selective material removal. These findings are further supported by post operando XPS, TEM and conductive AFM analyses. The dry-wet Q-ALE sequence was demonstrated on both PVD blanket and ALD-patterned tungsten wafers using existing 300-mm fab tools, achieving ~8 Å per cycle. These results highlight lab-to-fab scalability. More broadly, the combined dry-wet ALE framework provides a versatile platform for layer-by-layer etching of technologically important materials, particularly where purely wet oxidation is not self-limiting (or is chemically challenging), while wet removal offers strong oxide-to-metal selectivity.

8:30am **ALE1-TuM-3 Smooth Post-etch Morphology in Ligand Assisted Molybdenum Wet Atomic Layer Etch**, *Tulashi Dahal*, *Trace Hurd*, *Antonio Rotondaro*, Tokyo Electron America Inc.,

Molybdenum (Mo) has gained significant attention from semiconductor industries for its applications on logic BEOL, buried power rails, and 3 D NAND. Some of these applications require partial etch back of Mo where post-etch morphology is critical to device performance. Wet atomic layer etching offers material removal with Angstrom-level precision at or near room temperature and at ambient pressure by utilizing two sequential self-limiting steps. In the first step, the Mo surface is exposed to an oxidizing solution to form self-limiting surface passivation. In the second step, the modified Mo surface is selectively removed via dissolution in suitable chemistry. Etching of polycrystalline Mo is susceptible to surface roughness increase and uncontrolled etch rate due to solubilization of modified surface products in oxidizing solutions. Here, we present a novel method for controlled Mo etch with improved post-etch surface morphology via ligand assisted surface modification of metallic Mo in aqueous oxidizing solution. A ligand binds with the metal center to form a complex surface product that is insoluble in an aqueous oxidizing solution, preventing the continuous Mo background etch, and resulting in preserved post-etch surface smoothness.

Cyclic etch experiments were carried out by dipping Mo coupons in an oxidizing solution with varying ligand concentration followed by selective removal of modified layer in a low concentration dissolution chemistry. Mo etch rate decreases with increasing ligand concentration. The etch rate, however, can be enhanced via surface oxidation at an elevated temperature (Fig. 1). For the same ligand concentrations, Mo etch rate can be greatly improved by tuning the oxidizer concentration (Fig. 2). A significant enhancement in Mo etch rate [from ~0.12 nm/cycle with p% oxidizer +250 mM ligand to ~0.43 nm/cycle in 5p% oxidizer+250 mM ligand] with increased oxidizer concentrations suggests the formation of thicker surface oxide as surface passivation. For higher oxidizer concentration, Mo ER is independent of ligand concentrations under study (Fig. 2). The measured RMS roughness [ $\sim$  (0.63±0.04) nm] of the post-etch Mo coupon with higher ligand concentration is the same as RMS roughness of [ $\sim$  (0.62±0.03) nm] of

the reference coupon (Fig. 3). We attribute the preserved morphology in post-etch Mo coupon with higher ligand concentration to the suppression of continuous Mo etch due to the formation of a stable metal complex that is insoluble in oxidizing solution. The ability to remove Mo at a substantial rate with atomic-level precision and preserved surface morphology in post-etch coupons using less harsh oxidizer and ligand in an aqueous solution near room temperature may provide a cost-effective alternative solution to recess Mo in the industrial scale.

8:45am **ALE1-TuM-4 The Effect of the Angle of Incidence of Ions on Atomic Layer Etching**, *Joseph Vella*, TEL Technology Center America; *David Graves*, Princeton University

Plasma assisted atomic-layer etching (ALE) processing techniques have seen widespread usage in the semiconductor manufacturing industry. In its simplest form, an ALE process consists of two steps: a chemical modification step and a removal step. The removal step is often performed by exposing the substrate to a chemically inert plasma (such as an argon plasma) where energetic ions remove the modified surface. In much of the literature, it is assumed that a majority of the ions are hitting the surface at normal incidence, although there are some published results that examine the effect of the ion angle of incidence on ALE behavior. A fundamental understanding of any effect of the ion angle of incidence with in ALE processes is relevant to etching features into patterned surface (especially for high-aspect ratio features). In this work we utilize both classical molecular dynamics (MD) simulations and a reduced order model[1] (ROM) to build this understanding. We focus on the relatively simple case of silicon (Si) ALE by exposure to chlorine gas (Cl<sub>2</sub>) and argon ions (Ar<sup>+</sup>). We show how the angle of incidence of Ar<sup>+</sup> ions affects the etch per cycle (EPC), etch product distribution, and etch product selectivity.

#### References

[1] J. R. Vella, Q. Hao, M. A. I. Elgarhy, V. M. Donnelly, and D. B. Graves, "A Transient Site Balance Model for Atomic Layer Etching", *Plasma Sources Sci. Technol.*, 2024, 33, 075009.

9:00am **ALE1-TuM-5 Ab Initio Modeling of Atomistic Diffusion of Halogen Species at the Etching Front**, *Sangheon Lee*, Ewha Womans University, Republic of Korea

Halogen atoms play key roles in etching processes for semiconductors. Fluorocarbon or hydrofluorocarbon gases are commonly used for reactive-ion etching processes. When treated with plasma, these gases decompose and radicals migrate to the etching front. Halogen gases like Cl<sub>2</sub> are often used to treat metal or dielectric surfaces to form halogenated surfaces for atomic layer etching processes. Despite the well-established fact that etching does not proceed without halogen species, detailed surface reaction mechanisms involving halogens are rarely revealed. In this presentation, I will discuss mechanisms of halogen-mediated etching processes, focusing on atomistic diffusion of halogen species at dielectric and metal etching fronts. This work is based on state-of-the-art ab initio calculations combined with recent experimental results from my academic colleagues.

9:15am **ALE1-TuM-6 Quantum Chemistry Calculation for Predicting Salt By-Products in ALE Processes**, *Yuri Barsukov*, Lam Research Corp.; *Mingmei Wang*, *Thorsten Lill*, Lam Research Corporation

It is well established that during the thermal and plasma-assisted atomic layer etching of silicon nitride – a process widely used in the semiconductor industry – the main solid by-product is ammonia fluorosilicate (AFS) salt, if the feed gas contains both hydrogen and fluorine. In fact, such chemistries initially convert silicon nitride into AFS salt, which subsequently decomposes into gaseous by-products. During high-aspect ratio etching, the formation of AFS significantly affects the overall process performance by influencing critical characteristics such as etch rate, selectivity, and feature shape distortion, which are vital for semiconductor manufacturing.

Despite this, the thermodynamic properties of AFS – such as its decomposition temperature and the dependence of this temperature on pressure – have not been reliably determined. To address this gap, we performed calculations of standard Gibbs free energies for various crystalline structures of AFS using density functional theory (DFT). The distinctive feature of AFS is that this ionic salt decomposes and sublimates through distortion of ionic bonds, bypassing the liquid state; therefore, DFT level of approach is required to accurately describe such complex chemical bond transformations. The calculations show that the AFS decomposition temperature varies in a wide range depending on its crystal structure and decreases significantly with increasing water content, in agreement with our previous publication [1].

In addition, our simulations show that similar ionic salts with the similar properties – such as  $\text{NH}_4\text{F}$ ,  $\text{NH}_5\text{F}_2$ ,  $(\text{NH}_4)_2\text{SiF}_6 \cdot \text{NH}_4\text{F}$ ,  $\text{NH}_4\text{BCl}_3\text{F}$ ,  $(\text{NH}_4)_2\text{TiF}_6$ , and  $(\text{NO})_2\text{SiF}_6$  – can also form during etching. These compounds can be classified into reactive and unreactive salts. The simulations predict that some of these salts are stable only at temperatures below 0 °C. Given that low-temperature etching is an increasingly important direction in the semiconductor industry, such salts may play a more significant role in future etching processes.

[1] T. Lill *et al.*, “Low-temperature etching of silicon oxide and silicon nitride with hydrogen fluoride,” *Journal of Vacuum Science & Technology A*, vol. 42, no. 6, p. 063006, Dec. 2024, doi: 10.1116/6.0004019.

9:30am **ALE1-TuM-7 Influence of Oxide Phase and Surface Facet on Atomic Layer Etching of High-k Metal Oxides**, *Michael Nolan*, Tyndall Institute, Ireland; *Rita Mullins*, Tyndall National Institute, University College Cork, Ireland

Thermal Atomic Layer Etching (ALE) is of significant interest for its potential to deliver atomic level control over the etch of many materials, in particular in semiconductor device processing for use in future CMOS nodes with requirements for sub-nm levels of control on complex structures. It is performed using sequential surface modification and volatile release reactions with relevant precursors. For metal oxides, HF is the most widely used modifier. It fluorinates the initial surface to form a metal fluoride layer, leaving the remainder of the film unmodified. The modified, non-volatile layer undergoes ligand-exchange with a second precursors of which  $\text{TiCl}_4$  and  $\text{SiCl}_4$  are widely used. This volatilizes the MF<sub>4</sub> layer releasing product species. The question of the role of the phase and surface facets in a deposited high-k metal oxide film on thermal ALE has received insufficient attention to date but can be readily addressed with first principles atomistic simulations. In this contribution we use density functional theory simulations to explore the effect of the phase and surfaces of  $\text{HfO}_2$  and  $\text{ZrO}_2$  on the HF modification half-cycle of ALE. The models used in this study representing polycrystalline materials are the low energy (111) and (001) surface facets of monoclinic, orthorhombic and tetragonal  $\text{HfO}_2$  and  $\text{ZrO}_2$ . Our thermodynamic analysis shows that for polycrystalline  $\text{HfO}_2$  and  $\text{ZrO}_2$ , the HF pulse reacts in a self-limiting manner, and is favoured at temperatures typical of CMOS processing. The upper temperature limit is highly sensitive to the phase and surface of both oxides. Models of HF coverage are used to compute calculated theoretical etch rates for the different oxide phases and surface facets and these show a strong dependence on both the crystal phase and the surface so that if different phases and facets are present in a deposited high-k oxide, an uneven etch profile with increased roughness will be seen. The origin of this dependence arises from the stability, geometry and surface atomic coordination environments in the metal oxides.

9:45am **ALE1-TuM-8 Modeling  $\text{SiO}_2$  Atomic Layer Etching Using HF/ $\text{NH}_3$  Co-Dosing**, *Philipp Haslhofer*, *Tobias Reiter*, TU Wien, Austria; *Alexander Toifl*, *Andreas Hössinger*, Silvaco Europe Ltd., UK; *Lado Filipovic*, TU Wien, Austria  
Atomic Layer Etching (ALE) is a key process for achieving conformal and selective material removal in advanced semiconductor manufacturing, particularly for high-aspect-ratio (HAR) structures in 3D memory and logic devices. Owing to its self-limiting nature, ALE enables uniform etching over extended process times. However, predictive modeling of feature-scale behavior remains challenging due to the interplay of surface modification, diffusion, and volatile etching mechanisms.

In this work, we present a feature-scale simulation framework for cyclic ALE of  $\text{SiO}_2$  using HF/ $\text{NH}_3$  co-dosing in a chemical-oxide-removal (COR) process. The model is implemented in the in-house process simulator ViennaPS [1] and couples geometry-agnostic Monte Carlo ray tracing for gas-phase transport with a level-set method for surface evolution. During reactant pulses, precursor transport is modeled to be ballistic with cosine angular distributions, appropriate for plasma-less processes. Local surface fluxes obtained from ray tracing are converted into surface concentrations that drive surface reactions. Formation of ammonium fluorosilicate (AFS) is described using a parallel-resistance approach, enabling simultaneous treatment of surface-limited reactions and precursor diffusion-limited reactions through the modified layer. In addition, direct volatile etching of  $\text{SiO}_2$  by HF is incorporated via a thickness-dependent coverage function which activates under the conditions of incomplete AFS surface coverage.

Model parameters are calibrated against experimentally reported low-pressure-TEOS thickness data by Hagimoto *et al.* [2] for planar substrates over a range of precursor pulse times. The calibrated model is subsequently applied to HAR trench structures with aspect ratios up to 20 to investigate the influence of precursor partial pressures and sticking coefficients on etch

profiles. The simulations reveal transitions from stoichiometry-limited surface modification to diffusion-limited growth regimes, as well as the emergence of inverse aspect-ratio-dependent etching under asymmetric HF/ $\text{NH}_3$  sticking conditions, highlighting the sensitivity of ALE conformality to surface kinetics. To address the computational cost of simulating large numbers of ALE cycles, we introduce a cycle-skipping strategy in which surface concentrations are recalculated only after several cycles of constant-rate surface propagation. Comparison to gauge simulations, where surface concentrations are reevaluated for each ALE cycle, reveals that up to five cycles can be omitted while maintaining maximum profile deviations below 1% along the surface, corresponding to a significant reduction in computational cost.

Overall, the presented framework provides a physically motivated and geometry-agnostic approach for predictive ALE modeling in HAR structures capturing different reaction pathways and offers insight into the process windows governing conformality, selectivity, and throughput in HAR applications.

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