Atomic Layer Etching
Room Samda Hall - Session ALE1-TuA

ALE Tools & ALE Modeling

Moderator: Takayoshi Tsutsumi, Nagoya University

1:30pm **ALE1-TuA-1 Isotropic and Anisotropic ALE: Tool Aspects, Processes, and Applications**, ***Harm Knoops,*** Oxford Instruments Plasma Technology, UK **INVITED**

Applications' demands on control of etch depth, surface state, damage, and etching in 3D structures have caused atomic layer etching (ALE) to receive strong interest in recent years. One can distinguish ALE processes into two categories, isotropic and anisotropic processes. In this contribution, tool aspects, exemplary processes, and key applications for both isotropic and anisotropic ALE will be highlighted and, when appropriate, foundations and links between ALD and ALE will be addressed. Historically, tool designs for anisotropic ALE are built on those for reactive ion etching focusing on ion-energy control. Isotropic ALE processes are generally developed on ALD or ALD-like systems focusing on careful delivery and purging of precursor vapor at raised temperatures. To bring ALE to the next level, a closer look needs to be had at both the tool and process requirements. Among the general aspects important in the different steps in the ALE process are: control of plasma radical and ion fluxes and energies, delivery and removal of reactants and products from the chamber, process pressure and temperature (from ~350 ˚C down to cryogenic). For processes the discussion will range from BCl_3/Cl_2-Ar anisotropic chemistries to SF_6-$AlMe_3$ isotropic chemistries. Regarding applications, besides the well-known CMOS logic and 3D memory ones, power electronics, photonics, and quantum will be discussed. The aim being to highlight that control of interfaces and surfaces at the atomic scale is important even if the feature scale of the device is above ~100 nm. It is important to consider the different application spaces for ALE as this will also shape the requirements on tools and processes.

2:00pm **ALE1-TuA-3 Study on Plasma Induced Damaged Layer Formation Using Molecular Dynamics**, ***Junghwan Um,*** *Sung-Il Cho,* Samsung Electronics Co., Republic of Korea

Plasma etching is a key technology in semiconductor fabrication, enabling precise patterning at the nanoscale. However, plasma-surface interactions often lead to the formation of a damage layer, which can negatively impact material properties and device performance. Understanding the mechanisms of damage layer formation at the atomic scale is crucial for optimizing plasma etching conditions and minimizing unwanted effects.

In this study, we employ molecular dynamics (MD) simulations to investigate the fundamental processes involved in plasma-induced damage layer formation. The simulations focus on the effects of ion energy, ion species and surface chemistry on the evolution of the damage layer. By simulating energetic ion bombardment and its interactions with the substrate, we analyze structural modifications. Our results show that higher ion energy leads to deeper penetration of ions into the substrate, increasing the damage layer thickness. Low-energy ions, on the other hand, primarily cause surface modifications without significant subsurface damage. The choice of ion species also plays a critical role, with heavier ions inducing more structural disorder compared to lighter ions due to their higher momentum transfer. Furthermore, we examine the role of reactive species in plasma etching, such as fluorine (F) or chlorine (Cl), which contribute to both material removal and chemical modification of the substrate. The competition between physical sputtering and chemical etching is analyzed to determine the optimal conditions for achieving a damage-free etching process. By comparing MD simulation results with experimental findings, we establish a comprehensive understanding of plasma-induced damage mechanisms. Our study provides valuable insights into designing advanced plasma etching processes with minimized damage, which is essential for next-generation semiconductor devices. These findings can guide the development of new plasma processing strategies, including low-damage etching techniques and optimized plasma parameters for emerging nanofabrication applications.

2:15pm **ALE1-TuA-4 Theoretical Analysis on Crystalline Phase-Dependent Surface Fluorination of HfO_2 for Atomic Layer Etching**, ***Sujin Kwon,*** *Bonggeun Shong,* Hongik University, Republic of Korea

Hafnium oxide (HfO_2) thin films have garnered significant attention in microelectronics industry due to its high dielectric constant, and more recently, the ferroelectric (FE) properties of hafnium zirconium oxide (HZO). For applications of HfO_2 thin films, precise control of the thickness is necessary, and thus atomic layer deposition (ALD) and atomic layer etching (ALE) processes of HfO_2 can be crucial. Several ALE chemistry of HfO_2 are known, and most of them include fluorination of the surface using HF. While ALE is often believed to reduce roughness, some previous experimental reports indicate that the surface roughness of HZO thin films can increase after ALE [1]; additionally, the etch rates in ALE of HfO_2 and ZrO_2 are dependent on their crystallinity [2], which can be related to the propensity toward surface fluorination [3]. In this study, we investigate the variation of surface fluorination of HfO_2 according to its crystalline phases. The HF-based surface fluorination of four representative phases of HfO_2 – monoclinic, tetragonal, orthorhombic, and cubic – is explored. Using machine-learning interatomic potential (MLIP) calculations, Natarajan-Elliott (N-E) analyses on spontaneous etch (SE) versus self-limiting (SL) conditions of surface fluorination are performed [4]. Based on current results, it can be inferred that the variation in fluorination behaviors across different crystallinity and phases of the polycrystalline HfO_2 thin films may lead to increased surface roughness after ALE due to differences in etch rates.

Acknowledgments. This work was supported by Samsung Electronics.

References [1] Appl. Phys. Lett. 120, 122901 (2022), [2] J. Vac. Sci. Technol. A 38, 022608 (2020), [3] J. Vac. Sci. Technol. A 40, 022604 (2022), [4] Chem. Mater. 32(8), 3414-3426 (2020)

2:30pm **ALE1-TuA-5 Removal Reaction Mechanisms During Thermal Atomic Layer Etching of Aluminum Oxide: A First-Principles Study**, ***Khabib Khumaini,*** *Gyejun Cho, Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

Understanding the mechanism of atomic layer etching (ALE) is essential for process design and optimization. Thermal ALE of metal oxides typically involves surface fluorination followed by ligand exchange reactions to remove the fluorinated layer. In the removal step, surface fluorine groups are usually replaced by methyl groups or chlorine atoms to increase the volatility of the modified substrate using metal precursors. Surface reactions during the removal step of ALE aluminum oxide (Al_2O_3) using various metal precursors have been reported using *in situ* characterizations [1]. However, the investigation of the atomic-scale mechanism remains limited. Therefore, we performed density functional theory (DFT) calculations to study the removal reaction during ALE of Al_2O_3. Since the fluorination step produces an amorphous aluminum fluoride (a-AlF_3) layer, we constructed an amorphous substrate model by the melt-quench method and optimized the surface group density. Removal reactions with $Al(CH_3)_3$, $AlCl_3$, $AlCl(CH_3)_2$, $SiCl_4$, and $TiCl_4$ were then simulated. At 250°C, the removal of a-AlF_3 by $Al(CH_3)_3$ and $AlCl_3$, releasing $Al_2F_2(CH_3)_4$ and $Al_2F_2Cl_4$, occurs spontaneously with low activation energies of 1.08 and 0.85 eV, respectively. $AlCl(CH_3)_2$ preferentially removes a-AlF_3 with activation energies of 0.54–0.74 eV, which is lower than $Al(CH_3)_3$ and $AlCl_3$. Conversely, reactions with $SiCl_4$ or $TiCl_4$ release only $SiFCl_3$ or $TiFCl_3$ molecules with no release of aluminum-containing species, indicating that a-AlF_3 etching does not occur at 250°C. These results are in agreement with the experimental observations. Our DFT calculation results indicate that the substitution of a methyl group with a chlorine atom in the precursor increases the reactivity, while the substitution of aluminum with silicon and titanium significantly decreases both reactivity and spontaneity. These results will contribute to the rational design of precursors for thermal ALE processes.

[1] J.W. Clancey et al., J. Phys. Chem. C **124** (2020) 287–299.

2:45pm **ALE1-TuA-6 Multiscale Modeling of Gallium Nitride Atomic Layer Etching in Chlorinated Plasmas: A Combined Dynamic Global Model, Ab-initio and Kinetic Monte Carlo Approaches**, ***Tojo Rasoanarivo,*** *Cédric Mannequin, Isabelle Braems,* Institut des Matériaux de Nantes Jean Rouxel, France*; Fabrice Roqueta, Mohamed Boufnichel,* STMicroelectronics, France*; Ahmed Rhallabi,* Institut des Matériaux de Nantes Jean Rouxel, France

Plasma Atomic Layer Etching (ALE) is a cyclic etching process for which one cycle relies on two self-limited half-reactions, separated by purges. An ideal ALE cycle comprises an adsorption step to modify the outermost surface layer, followed by an activation step to selectively remove the aforementioned modified layer without etching the underlying non-modified layers, thereby achieving atomic-scale resolution. The ALE of GaN using alternating Cl_2 and Ar plasma for the adsorption and activation steps, respectively, has been the subject of extensive research [1]. These studies suggest that the adsorption step relies on surface modification by chlorine radicals, while the activation step is achieved by selectively controlling the

energy of ionic bombardment. However, the majority of ALE research has been conducted through experimental approaches, with some modeling studies employing molecular dynamics for common materials such as silica-based substrates [2].

In this study, we propose a multiscale kinetic model of GaN ALE in chlorinated plasmas. The temporal evolution of precursors fluxes during ALE cycles is provided by a dynamic global model of chlorinated plasmas [3]. The interactions between chlorine species and the GaN surface are investigated through the use of Density Functional Theory (DFT), while ion bombardments are consequently calculated using the Stopping and Range of Ions in Matter software (SRIM) considering the ion energy and angular distributions induced by the sheath at the interface between the plasma and the surface. Thereafter, those results are implemented in our new kinetic Monte-Carlo etching model with an atomic scale description. The simulation results demonstrate the effects of machine parameters (pulse lengths, flow rates, pressure, RF power) on the plasma composition, the etched depth and the etched GaN surface morphology at each ALE cycle.

Our approach is less time-consuming than molecular dynamics or DFT-only methods for atomic layer etching processes while following entire processes. Its suitability to a wide range of ALE recipes, for instance purge-free processes, could offer insights for process optimization.

References

[1] Mannequin, Vallée, Akimoto, Chevolleau, et al., JVST A, (2020)
[2] Kounis-Melas, Vella, Panagiotopoulos, Graves, JVST A, (2025)
[3] Rasoanarivo, Mannequin, Roqueta, Boufnichel, Rhallabi, JVST A, (2024)

3:00pm **ALE1-TuA-7 Characteristics of the Power Delivery System of Transformer-Coupled Plasma Source for Remote Plasma Process in Semiconductor Manufacturing**, *Tae S. Cho, **Hakmin Kim**, Giwon Shin, Jaehoon Choi, Sooyoung Hwang, Jihyun Kim,* Wonik IPS, Republic of Korea

As the semiconductor industry progresses with sub-10 nm features, 3D stacked architectures, and intricate gate-all-around structures, the demand for remote plasma technologies has grown significantly. The requirements for the remote plasma are to generate a high density of radicals at low power and deliver them to the wafer processing region with minimal loss during transport, while preventing damage to the wafer from ion bombardment. "We have conducted an analysis of the power delivery system of the transformer-coupled plasma (TCP), which is one of the most commonly used plasma sources that meets these requirements. Since the power efficiency of the TCP directly influences the plasma properties, understanding the power transfer characteristics is crucial for improving process stability and uniformity."

The model was expressed as a function of the number of ferrite cores and dielectric breaks, that are the primary components of the TCP. The model was experimentally validated by varying the number of ferrites and breaks in the TCP, and it was confirmed that the experimental results were in good agreement with the values predicted by the model. Therefore, the proposed model was able to effectively predict the characteristics of the power delivery system of the TCP source. In future work, we aim to derive a more accurate equivalent model and a generalized equation by incorporating variables related to the plasma properties

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