

## Atomic Scale Processing Mini-Symposium Room 116 - Session AP2+EM+PS+TF-MoA

### Modeling and Simulations of Atomic Layer Processing

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Greg Parsons, North Carolina State University

#### 4:00pm AP2+EM+PS+TF-MoA-11 Atomistic Simulations on the Fundamental Aspects of Atomic Layer Processing (ALP), *Bonggeun Shong*, Hongik University, Republic of Korea **INVITED**

As size of electronic devices are miniaturized to nanoscale, the precision of their fabrication processes is becoming extremely demanding. Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on sequential, self-limiting surface reactions. Through ALD, high conformality on high-aspect ratio substrates, thickness control at the Angstrom level, and tunable film composition are achievable. Furthermore, area-selective ALD (AS-ALD) has recently emerged as a possible alternative bottom-up approach for nanoscale patterning. With these advantages, ALD is gaining interest as a powerful tool for many industrial and research applications, especially in microelectronic fabrication. Furthermore, atomic layer etching (ALE) is emerging as a novel technique that can provide atomically controlled etching of materials. These technologies with atomic layer precision are often altogether referred to as atomic layer processing (ALP). Ideally, the entire ALP processes are based only on the surface chemistry of the substrates. Thus, it is important to understand their surface reaction mechanisms in order to improve the process conditions and material quality, and even to design novel materials and processes. With development of modern simulation tools, utilization of atomistic calculations is becoming increasingly useful toward deeper understanding and design of such chemical reactions. However, ALD processes often face limitations toward fabrication of next-generation semiconductor devices due to their size scale and structural complexity; furthermore, such problems are often convoluted with challenges toward realistic simulations of surface chemical processes. In this talk, analysis of fundamental surface chemistry of various ALP based on computational chemistry methods, as well as development of new processes and materials based on chemical simulations will be presented.

#### 4:30pm AP2+EM+PS+TF-MoA-13 Understanding Process Parameters in High-Aspect-Ratio ALD via Transport Modeling, *Victor Vogt*, University of Michigan; *A. Gayle*, National Institute of Standards and Technology (NIST); *A. Miranda Manon*, *A. Lenert*, *N. Dasgupta*, University of Michigan

Atomic layer deposition (ALD) is a powerful tool to modify ultra-high-aspect-ratio structures with unparalleled conformality. We have recently demonstrated the ability of ALD to modify silica aerogels with aspect ratios greater than 60,000:1 and improve their thermal stability from ~600°C to ~800°C, for applications in concentrating solar thermal energy generation.<sup>1</sup> To facilitate conformal ALD modifications on these extreme aspect ratios, a reaction-diffusion model was developed to precisely predict infiltration into the aerogel as a function of exposure time and number of doses, enabling tunable control of the infiltration depth.<sup>2</sup>

In this study, we have built upon our previous reaction-diffusion model to explore the effects of exposure time, precursor temperature, and number of aerogels coated on process time and precursor utilization. We analyze process parameter trends in terms of the governing reaction-diffusion mechanism and relevant equations. These trends are then validated experimentally via energy dispersive x-ray spectroscopy (EDS) mapping of the infiltration depth. Additionally, we explore the relationship between number of aerogels coated and reactor volume, and we analyze the impacts of this on ALD reactor design for high-aspect-ratio substrates. Finally, we demonstrate that ALD can be used to tune the mechanical strength and stiffness of silica aerogels, a key limitation of these materials in practical applications. This work will enable a greater understanding of high-aspect-ratio ALD processing as well as its potential applications in the modification of porous materials.

References:

<sup>1</sup> Z.J. Berquist, A.J. Gayle, N.P. Dasgupta, and A. Lenert, Transparent Refractory Aerogels for Efficient Spectral Control in High-Temperature Solar Power Generation. *Adv. Funct. Mater.* **2022** 32, 2108774.

<sup>2</sup> A.J. Gayle, Z.J. Berquist, Y. Chen, A.J. Hill, J.Y. Hoffman, A.R. Bielinski, A. Lenert, and N.P. Dasgupta, Tunable Atomic Layer Deposition into Ultra-High-

Aspect-Ratio (>60000:1) Aerogel Monoliths Enabled by Transport Modeling, *Chem. Mater.* **2021** 33 (14), 5572-5583.

#### 4:45pm AP2+EM+PS+TF-MoA-14 Modeling Remote Inductively Coupled Plasmas for Plasma-Enhanced Atomic Layer Deposition, *Mackenzie Meyer*, *D. Boris*, *M. Johnson*, *J. Woodward*, *V. Wheeler*, US Naval Research Laboratory; *M. Kushner*, University of Michigan, Ann Arbor; *S. Walton*, US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) uses a plasma step to generate the necessary reactive species, allowing atomic layer deposition (ALD) processes to occur at lower temperatures and with additional reaction chemistries compared to thermal ALD. Remote inductively coupled plasma (ICP) sources are often used in PEALD as they limit electrons and ions at the growth substrate while providing radicals from the plasma. However, remote ICP systems, particularly downstream of the source, are not fully understood. Modeling of remote ICPs can contribute to an understanding of these systems. In this work, modeling of remote ICPs is performed using the 2D Hybrid Plasma Equipment Model (HPeM). The remote ICPs are based on the Veeco Fiji G1 and G2 sources operating in an N<sub>2</sub>/Ar mixture. Both inductively and capacitively coupled power contribute to the power deposited into the plasma. The results of the model are compared to experimental measurements reported, including atomic N density in the plasma source and electron density and plasma potential downstream in the spatial afterglow of the ICP. The model is also used to examine the production of species that are not measured, including metastable N<sub>2</sub>, as well as the absolute and relative fluxes of reactive species to the substrate, for a range of operating conditions. The results are then linked to the growth of nitride films in an effort to quantify the relative importance of different operating modes and reactive species. This work is partially supported by the Naval Research Laboratory base program.

#### 5:00pm AP2+EM+PS+TF-MoA-15 Prediction of Plasma-induced Changes in Surface Morphology and Composition during Atomic Layer Deposition: A Combined Ab-Initio and Monte Carlo Approach, *G. Hwang*, *Ting-Ya Wang*, University of Texas at Austin

Atomic layer deposition (ALD) has emerged as a method offering enhanced precision and control in comparison to traditional chemical vapor deposition. It operates through alternating cycles of two half-cycle reactions, ensuring sequential and self-limiting deposition. However, thermal ALD necessitates high deposition temperatures (> 400 °C), particularly for nitridation. Although employing plasma can reduce these surface temperatures, plasma can have detrimental effects on materials too, including modification of the chemical composition and densification, which profoundly impact crucial material properties such as dielectric constant.

Therefore, understanding the plasma-induced changes in surface morphology and composition is crucial. However, existing experimental techniques encounter limitations in surface analysis. Non-polar bonds, such as N<sub>2</sub> dimer, are inactive under infrared (IR) spectroscopy. X-ray photoelectron spectroscopy causes surface damage to a certain extent. Moreover, overlapping signals may render the analysis uncertain and challenging. Theoretical methods have their own set of limitations. Molecular dynamics (MD) simulations allow the study of dynamic processes but are constrained by limitations in both length and time scales, which make it unsuitable for ALD systems, where primary reactions fall into the category of rare events.

The integration of kinetic Monte Carlo (kMC) with density functional theory (DFT) presents a promising simulation approach for ALD. However, a notable challenge lies within kMC, specifically the requirement for a predefined list of permissible events. Traditionally, researchers identify a set of reactions considered most significant. Yet, given the numerous potential events occurring on a surface and the criticality of rare events in ALD, outcomes derived from a manually compiled list may sometimes lack authenticity.

We developed an atomistic, off-lattice, and three-dimensional simulator that integrates kMC and DFT, and employed a strategic approach to formulate a comprehensive event list, with the goal of encompassing a wide range of potential surface reactions. Our investigation centered on assessing the effects of N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> plasmas on SiCN material, including examination of the roles played by radicals and ion bombardment. Furthermore, we also studied the influence of process conditions, including temperature and pressure, while also analyzing the influence of oxygen exposure.

# Monday Afternoon, November 4, 2024

5:15pm AP2+EM+PS+TF-MoA-16 Modelling and Simulation of Plasma-Enhanced Atomic Layer Deposition of Silicon Nitride Over Sidewall Surfaces of a Closing Narrow-Gap Trench, *Jomar Tercero, K. Ikuse, S. Hamaguchi*, Osaka University, Japan

Molecular dynamics (MD) simulations were performed to study the transport mechanisms of chlorine (Cl) atoms during the plasma-enhanced atomic layer deposition (PE-ALD) of silicon nitride (SiN). PE-ALD is a technique to deposit highly precise and uniform thin films required for nanoscale semiconductor devices. The typical PE-ALD process involves sequential and self-limiting surface reactions, facilitating the formation of monolayers in a layer-by-layer manner.[1] In the case of SiN PE-ALD, chlorosilanes such as  $\text{SiH}_2\text{Cl}_2$  are commonly used as Si-containing gas precursors. During the first half-cycle, Si atoms of the precursors adsorb on the surface, whose surface atoms are then terminated by Cl atoms. Subsequently, the surface is exposed to nitrogen (N) and hydrogen (H)-containing plasmas. During this second half-cycle, H atoms react and capture Cl atoms on the surface, forming volatile hydrogen chloride (HCl) molecules.[2] In this study, our focus is PE-ALD of SiN over a trench structure when the gap is closing and the two facing sidewalls are approaching each other. In the desorption/nitridation half-cycle, Cl atoms must be removed from the extremely narrow gap by Cl or HCl diffusion if the gap is closing. The diffusion coefficients of Cl atoms in such narrow gaps were evaluated from molecular dynamics (MD) simulations, under different conditions for the surface temperature (700, 800, and 900 K), gap distance (0.6, 1, and 2 nm), and H density. The MD simulations revealed that, without H atoms, Cl diffusion was highly restricted. H atoms were observed to capture Cl atoms, assisting their transport in the narrow gap. Additionally, we observed the formation of  $\text{H}_2$  molecules, some of which penetrated the SiN bulk and diffused. The results indicate that, as the two facing SiN sidewalls approach each other and the gap diminishes, the transport of atoms and molecules in the gap becomes restricted and therefore the ALE process slows down, eventually forming a seam between the two facing sidewalls.

## References

- [1] K. Arts, S. Hamaguchi, T. Ito, K. Karahashi, H. C. M. Knoop, A. J. M. Mackus, and W. M. E. Kessels, "Foundations of atomic-level plasma processing in nanoelectronics," *Plasma Sources Science and Technology*, 31, 103002 (2022).
- [2] R. A. Ovanesyan, E. A. Filatova, S. D. Elliott, D. M. Hausmann, D. C. Smith, and S. Agarwal, "Atomic layer deposition of silicon-based dielectrics for semiconductor manufacturing: Current status and future outlook", *Journal of Vacuum Science and Technology A*, 37, 060904 (2019).

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