

Emerging Materials and Processes

Room Tampa Bay Salons 1-2 - Session EM1-TuM

Molecular Layer Deposition/Hybrid ALD

Moderators: Haripin Chandra, The Electronics business of Merck KGaA Darmstadt, Keith Wong, Applied Materials

8:00am **EM1-TuM-1 ALD Outstanding Presentation Award Finalist: The Impacts of Organic Structures on the Sensitivity of Molecular Atomic Layer Deposited EUV Resist Thin Films**, Thi Thu Huong Chu, Dan Le, University of Texas at Dallas; Markus Langer, Gregrey Swieca, University of Mississippi; Doo San Kim, Minjong Lee, Dushyant Narayan, University of Texas at Dallas; Nikhil Tiwale, Brookhaven National Laboratory; Jean-Francois Veyan, University of Texas at Dallas; Michael Eller, University of Mississippi; Chang-Yong Nam, Brookhaven National Laboratory; Jiyoung Kim, University of Texas at Dallas

Until now, the development of advanced hybrid EUV resists has largely emphasized inorganic metals with high EUV absorption, while the contribution of organic components remains insufficiently explored. In this work, we investigate how organic backbone structures influence the sensitivity and patterning performance of EUV resist materials, focusing on resist thin films synthesized via molecular atomic layer deposition (MALD) for next-generation EUV lithography. Under EUV exposure, negative tone MALD resist thin films consistently show that organic moieties with an aliphatic chain-based backbone exhibit enhanced sensitivity and improved patterning performance compared with those featuring an aromatic backbone.

To elucidate the underlying mechanisms responsible for the observed enhancement, various material characterization techniques, including in situ FTIR, XPS, Raman, and NP-SIMS, were conducted for two Zn-based systems that feature either organic with an aliphatic chain backbone [e.g., 2,3-dimercapto-1-propanol (DMP)], or an aromatic backbone [e.g., 4-mercaptophenol (4-MP)]. IR measurements, obtained from the in-situ FTIR system equipped with an electron flood gun, indicate clear changes in the aromatic ring of 4 MP upon electron exposure, reflected by a decrease in C=C bond. Additional material characterizations further confirm the changes in the aromatic ring and suggest the formation of graphitic-like carbon within 4-MP-based resist materials upon electron exposures. In contrast, while IR measurements of DMP-based resist thin films show evidence of new species formation, as indicated by an increase in various carbon species, NP-SIMS suggests changes in the oxidation state of Zn within DMP-based resist thin films.

Based on these material characterizations, we propose two distinct exposure mechanisms that potentially govern the sensitivity and patterning behavior of Zn/4-MP and Zn/DMP resist thin films. For the aromatic-based system, the organic moiety likely undergoes crosslinking, leading to the formation of a graphitic-like carbon network, whereas the aliphatic chain-based organic forms complex structures with the metal core surrounded by ligands. These findings provide critical guidance for the molecular design of MALD EUV resist thin films, enabling a balance between sensitivity and pattern fidelity to meet next-generation lithography performance targets.

This work is supported by the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. This research is also partially supported by the National R&D program (2022M3H4A3052556) through the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT in Korea.

8:30am **EM1-TuM-3 All-Dry-Processed Zn-Based Inorganic–Organic Hybrid Photoresists for EUV Lithography**, Thi Thu Huong Chu, Dan N. Le, Dushyant M. Narayan, Minjong Lee, Doo San Kim, University of Texas at Dallas; Nikhil Tiwale, Chang-Yong Nam, Brookhaven National Laboratory; Jiyoung Kim, University of Texas at Dallas

Extreme ultraviolet (EUV) lithography is the key enabling technology for sub-10 nm metal half-pitch semiconductor nodes.¹ However, one of the primary bottlenecks lies in the development step of the lithography process. Conventional wet development often leads to pattern collapse due to capillary forces generated during solvent evaporation.^{2,3} Although this issue is less severe in high- and hyper-NA EUV lithography as a result of reduced resist thickness, wet development can still degrade pattern fidelity through solvent-induced swelling, non-uniform dissolution, and surface-tension-driven stochastic effects, thereby increasing LER and defectivity.

To address these challenges, dry development processes are emerging as a promising alternative, eliminating the patterning issues associated with wet developers and their associated environmental costs. Here, we present a dry development approach of the Zn-based hybrid inorganic–organic resist systems deposited by molecular layer deposition (MLD). The resist films were patterned using both low-energy electron-beam lithography (100 V EBL) and EUVL. Dry development was then carried out by chemical vapor exposure to hexafluoroacetone (hfacH), which reacts with the Zn-based resists, generating volatile products such as Zn(hfac)₂ and organic by-products. During wet development, resist–developer interactions cause lift-off problems that hinder accurate sensitivity evaluation, and high-resolution patterning is degraded by resist swelling and spreading. In contrast, the dry development process achieves a tenfold improvement in sensitivity over wet development while resolving features as small as 10 nm with EUVL. This demonstrates the strong resistance of the exposed regions to hfacH vapor and the elimination of capillary-induced collapse, enabling controlled material removal without the limitations of liquid immersion. Among currently reported all-dry-processed EUV resists, we achieved a low critical dose of 27 mJ/cm² with a comparable LER of 1.6 nm.

These findings demonstrate a significant step toward realizing an all-dry EUV resist platform. By combining MLD-based hybrid resist materials with vapor-phase development, this approach not only mitigates fundamental limitations of wet processing but also opens pathways for scalable, high-performance patterning required for next-generation semiconductor manufacturing.

This work is supported by the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. This research is also partially supported by the National R&D program (2022M3H4A3052556) through the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT in Korea.

[1] I. Giannopoulos *et al.*, *Nanoscale*, **2024**, 16, 15533–15543.

[2] T. S. Kulmala *et al.*, *Proc. SPIE*, **2016**, 9776, 97762N.

[3] N. Kenane *et al.*, *J. Photopolym. Sci. Technol.*, **2024**, 37, 257–262.

8:45am **EM1-TuM-4 Polyurea Molecular Layer Deposition using Low Melting Point Precursors for Use in Biosensor Design**, Jay Werner, Seancarlos Gonzalez, David Bergsman, University of Washington

Molecular layer deposition (MLD) is a promising tool that can take the place of silane-based SAMs in some surface functionalization applications where a multilayer film is acceptable and a precise, conformal film thickness is desirable, such as in biosensor design. However, many organic MLD precursors have low vapor pressure or are solids at room temperature, which can lead to increased purge times and the possibility of condensation-induced valve clogging. This work presents an underexplored polyurea MLD chemistry using 2,4-toluene diisocyanate (TDIC) and ethylene diamine (ED). This process has some benefits over the similar and more common 1,4-phenylene diisocyanate (PDIC) reactant, such as reduced cost and lower melting point (and thus higher vapor pressure at room temperature). Film characterization suggests that this process is similarly well-behaved to PDIC-based polyurea: in situ ellipsometry shows that the process is both linear up to 55 cycles and self-saturating, XPS analysis shows the expected atomic ratio of oxygen and nitrogen in the film, and FTIR shows amide I & II peaks characteristic of polyurea. In addition, the films were analyzed using zeta potential analysis, fluorescence tagging, and water contact angle (WCA) goniometry to characterize their suitability for use in biosensor design.

9:00am **EM1-TuM-5 Conformality of Molecular Layer Deposited Polyurea for Sidewall Passivation**, Wallis Scholl, Colorado School of Mines; Thorsten Lill, Mingmei Wang, Wenyu Zhang, Louis Kim, Harmeet Singh, Lam Research Corporation; Sumit Agarwal, Colorado School of Mines

As the semiconductor industry transitions from fluorocarbon plasma chemistries to carbon-free reactive plasmas, new techniques are needed to passivate the sidewalls of high aspect-ratio (HAR) features during etch. Molecular layer deposition (MLD) is a vapor-phase thin film growth technique comprised of alternating surface reactions for deposition of organic and hybrid organic-inorganic chemistries. While MLD is an analogous technique to atomic layer deposition (ALD), the growth mechanism of MLD has added complexity due to the possibility of double reaction of both functional groups in the precursor molecule with the growth surface and physisorption of molecules into the film. Previous work on ALD has found that conformal deposition on HAR features requires very high precursor doses to supply necessary diffusive flow. However, we have

found that MLD polyurea films are surprisingly conformal using the saturation doses for a flat surface.

Polyurea was deposited via MLD using toluene diisocyanate and ethylene diamine as precursors. Figure 1 a) and b) shows scanning electron microscopy (SEM) images of AR~65:1 holes in SiO₂-SiN_x stacks, both with and without ~10 nm of polyurea deposited via MLD. The chips were then exposed to an etching plasma and imaged again [see Figure 1 c) and d)], and the presence of polyurea was found to result in a smaller CD throughout the entire feature. This result shows that during MLD, polyurea was deposited throughout the entire hole and then was able to protect the sidewalls during etch. We have attributed the unexpectedly high conformality of MLD to the physisorption contribution to film growth which we have shown in detail in previous work. This physisorbed material is free to diffuse throughout the film, which may assist in deposition at the bottom of the hole. However, the process must be carefully designed with this effect in mind, as physisorbed molecules can also diffuse out of the film, resulting in chemical vapor deposition when precursor molecules react in the gas phase. Further, we have studied the plasma-surface interactions of polyurea with HF plasma and shown that polyurea can act as a sacrificial layer during HF etch. When polyurea was deposited on top of SiO₂ or SiN_x and then exposed to an HF plasma, only the polyurea film was etched during initial plasma exposure, while the underlying material was protected. Only once the polyurea was completely consumed by reaction was SiO₂/SiN_x etch observed (see Figure 2). This work presents a new technique for sidewall passivation during HF etch.

9:15am EM1-TuM-6 Molecular Layer Deposition of Polyamide Membranes for Selective Water and Ion Transport, Ruoke Cai, 21 Kiryat Technion, Israel; *Brian Welch, Aleksandr Ershov, Jay P. Singh*, Technion Israel Institute of Technology, Israel; *Jeremiah W. Woodcock, Christopher Stafford*, NIST; *Kirti Sankhala*, Indian Institute of Technology Jodhpur, India; *Guy Ramon, Razi Epsztein, Viatcheslav Freger, Tamar Segal-Peretz*, Technion Israel Institute of Technology, Israel

Molecular Layer Deposition (MLD) offers atomic-scale precision for fabricating organic and hybrid materials, yet its applications in membrane technology remains relatively underexplored. Nanofiltration (NF) and reverse osmosis (RO) are critical techniques in desalination and water treatment, addressing the growing challenges of water scarcity. Conventional interfacial polymerization relies on rapid, diffusion limited reactions that produce structurally heterogeneity, and presence of sub-nanometer defects that limit membrane selectivity.

Here, we explore MLD as a new platform for fabricating polyamide-based filtration membranes, utilizing MLD precision for creating homogenous, defect-free high-performance filtration membranes. MLD RO membrane with an optimized thickness of 12 nm exhibited a twofold improvement in H₂O/NaCl selectivity compared to commercial desalination membranes. In addition, the defect-free nature of these membranes further enables probing the intrinsic properties of polyamide. MLD NF membrane display narrow effective pore size distributions and pronounced monovalent-divalent ion discrimination in both cation (Li⁺/Mg²⁺) and anion (Cl⁻/SO₄²⁻) separations. Overall, this work establishes MLD as versatile platform for fabricating angstrom-precise polyamide membrane, providing new opportunities to design next-generation filtration membranes for advanced water and ion transport.

9:30am EM1-TuM-7 Cyclic Siloxane Precursor for Molecular Layer Deposition of Polymer Networks, Sanne Deijkers, Peter Gordon, Seán Barry, Carleton University, Canada

Phosphane-ene polymer networks, typically made in bulk phase synthesis, are known for their oxygen scavenging properties, making them ideal as protective layers. Molecular layer deposition (MLD) of polymer networks offers the opportunity to engineer thin film polymer networks for flexible electronics, sensors, and other applications. MLD of phosphane-ene was demonstrated using the cyclic siloxane precursor tetramethyltetravinylcyclotetrasiloxane (D₄^{Vinyl}), isobutylphosphine (*i*BuPH₂), and an Ar plasma to generate P radicals to act as a cross-linking agent [1]. The D₄^{Vinyl} ring can remain intact and improve crosslinking in the MLD film, which is what our group proposed and what happens during the phosphane-ene MLD process [1], while the Knez group suggested ring opening in their work on MLD of siloxane-alumina films [2,3]. In this work, various growth mechanisms of polymer networks using the cyclic D₄^{Vinyl} precursor have been studied.

It was found that a long-lived radical is crucial to provide cross-linking. Switching from the primary phosphine *i*BuPH₂ to a primary amine *t*BuNH₂ did not result in growth. *In situ* quartz crystal microbalance (QCM)

displayed pulsing of the precursors, but no mass gain was observed. The short-lived N radical proved to be unsuitable for MLD of polymer networks through radical-mediated cross-linking.

The deposition reaction mechanisms of phosphane-ene MLD were examined. *In situ* cycle-by-cycle QCM was combined with *ex situ* ellipsometry, atomic force microscopy, and Fourier transform infrared spectroscopy. Together, it can be hypothesized that the reaction mechanism of D₄^{Vinyl} is dependent on the surface chemistry. The presence of a radical species versus a metal atom at the surface decides the favorability of ring-opening, with the π-acid nature of the metal playing a significant role in ring opening. This presentation will detail different mechanisms using the D₄^{Vinyl} precursor and discuss its implications on film density.

[1] J. T. Lomax *et al.*, *Chem. Mater.*, 35, 4, 2023

[2] K. Ashurbekova *et al.*, *Chem. Mater.*, 33, 3, 2021

[3] K. Ashurbekova *et al.*, *Chem. Commun.*, 57, 17, 2021

9:45am EM1-TuM-8 Extreme Ultraviolet and Electron Beam-Induced Decarboxylation of Hybrid MLD Aluminum Oxalate Photoresists, Long Viet Than, Stanford University; *Miso Kim*, Hongik University, Republic of Korea; *Oleg Kostko*, Lawrence Berkeley National Laboratory (LBNL); *Bonggeun Shong*, Hongik University, Republic of Korea; *Stacey F Bent*, Stanford University

Continued device scaling with the introduction of high numerical aperture (NA) extreme ultraviolet (EUV) lithography will require innovations in photoresist materials. Particularly, new resist chemistries are needed to address the photon and material stochastic challenges that define the current resolution limit. Molecular layer deposited (MLD) metal-organic photoresists offer intrinsic advantages in precise thickness control and chemical homogeneity that can address some of these challenges. However, many MLD resists have poor EUV and electron beam sensitivity, leading to the need to explore new molecular designs that better harness the reactions induced by EUV-generated electrons.

In this work, we introduce a rationally designed MLD resist utilizing metal carboxylate groups to provide an efficient solubility switch mechanism by using trimethylaluminum (TMA) and oxalic acid precursors to deposit aluminum oxalate thin films. X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy reveal their chemical structure, showing that the metal oxalate coordination network reorganizes during exposure to air. We investigate the resist patterning mechanism and performance via electron beam lithography and flood EUV exposure. We use XPS and atomic force microscopy (AFM) to study post-e-beam chemical changes and film shrinkage, and *in situ* residual gas analysis and total electron yield measurements to identify reactions occurring during EUV exposure. Results show that exposure-induced decarboxylation results in CO/CO₂ gas evolution, inorganic Al-O bonding, and negative tone patterning. The photoresist can be developed with water, yielding an e-beam sensitivity of ~8500 μC/cm² (at 100 keV accelerating voltage) and EUV sensitivity of ~200 mJ/cm² – among the best for Al-based resists in the literature. Using electron beam lithography, line/space patterns as small as 14 nm half pitch are resolvable, with a line width roughness (LWR) of 5.2 nm. Thus, this work provides a new chemical motif applicable to hybrid MLD photoresists and highlights the importance of the organic ligand in determining the efficiency of the patterning mechanism.

Author Index

Bold page numbers indicate presenter

— A —

Agarwal, Sumit: EM1-TuM-5, 1

— B —

Barry, Seán: EM1-TuM-7, 2

Bent, Stacey F: EM1-TuM-8, 2

Bergsman, David: EM1-TuM-4, **1**

— C —

Cai, Ruoke: EM1-TuM-6, **2**

Chu, Thi Thu Huong: EM1-TuM-1, 1; EM1-TuM-3, **1**

— D —

Deijkers, Sanne: EM1-TuM-7, **2**

— E —

Eller, Michael: EM1-TuM-1, 1

Epsztein, Razi: EM1-TuM-6, 2

Ershov, Aleksandr: EM1-TuM-6, 2

— F —

Frager, Viatcheslav: EM1-TuM-6, 2

— G —

Gonzalez, Seancarlos: EM1-TuM-4, 1

Gordon, Peter: EM1-TuM-7, 2

— K —

Kim, Doo San: EM1-TuM-1, 1; EM1-TuM-3, 1

Kim, Jiyoung: EM1-TuM-1, **1**; EM1-TuM-3, 1

Kim, Louis: EM1-TuM-5, 1

Kim, Miso: EM1-TuM-8, 2

Kostko, Oleg: EM1-TuM-8, 2

— L —

Langer, Markus: EM1-TuM-1, 1

Le, Dan: EM1-TuM-1, 1

Lee, Minjong: EM1-TuM-1, 1; EM1-TuM-3, 1

Lill, Thorsten: EM1-TuM-5, 1

— M —

M. Narayan, Dushyant: EM1-TuM-3, 1

— N —

N. Le, Dan: EM1-TuM-3, 1

Nam, Chang-Yong: EM1-TuM-1, 1; EM1-TuM-3, 1

Narayan, Dushyant: EM1-TuM-1, 1

— R —

Ramon, Guy: EM1-TuM-6, 2

— S —

Sankhala, Kirti: EM1-TuM-6, 2

Scholl, Wallis: EM1-TuM-5, **1**

Segal-Peretz, Tamar: EM1-TuM-6, 2

Shong, Bonggeun: EM1-TuM-8, 2

Singh, Harmeet: EM1-TuM-5, 1

Singh, Jay P.: EM1-TuM-6, 2

Stafford, Christopher: EM1-TuM-6, 2

Swieca, Gregrey: EM1-TuM-1, 1

— T —

Than, Long Viet: EM1-TuM-8, **2**

Tiwale, Nikhil: EM1-TuM-1, 1; EM1-TuM-3, 1

— V —

Veyan, Jean-Francois: EM1-TuM-1, 1

— W —

Wang, Mingmei: EM1-TuM-5, 1

Welch, Brian: EM1-TuM-6, 2

Werner, Jay: EM1-TuM-4, 1

Woodcock, Jeremiah W.: EM1-TuM-6, 2

— Z —

Zhang, Wenyu: EM1-TuM-5, 1