Emerging Materials

Room Tamna Hall BC - Session EM-TuA

Molecular Layer Deposition & Hybrid Materials II

Moderators: Jolien Dendooven, Ghent University, Belgium, **Chang-Yong Nam**, Brookhaven National Laboratory

1:30pm **EM-TuA-1 Vapor Phase Infiltration for Membrane Modification***, **David Bergsman,*** University of Washington **INVITED**

Membrane filtration is a promising tool for reducing energy consumption and carbon emissions in areas like industrial manufacturing, food and beverage, municipal water treatment, and pharmaceuticals. However, improvements to membrane permeability, selectivity, thermal stability, chemical stability, and fouling resistance will be required before they are cost-effective enough to handle the acidic, alkaline, organic, and otherwise complex feed streams present in many applications. Of the commercial membranes commonly available, polymeric membranes are relatively low cost but often suffer from low thermal and chemical stability, while other membrane materials can be difficult or expensive to manufacture. Vapor phase infiltration (VPI), also known as sequential infiltration synthesis or atomic layer infiltration, is one potential cost-effective strategy for making higher-performance membranes. In VPI, a polymer is exposed to vapor phase metal-organic reactants which absorb, diffuse, and react in the polymer to form a composite material. This approach could be used to upgrade existing membranes through post-synthetic modification to improve their performance. However, more work is needed to understand the impact of this process on polymer properties and to discover new materials that best enable the wider implementation of membrane separations. This presentation will highlight our work to apply the VPI process to membrane separations. We will review examples of how we have used VPI to improve the conductivity of membranes through the formation of laser induced graphene, our work to understand the trade-off between infiltration and polymer toughness, and our exploration of organic reactants that could expand the library of infiltration processes. In doing so, this presentation will showcase the potential of VPI to create next-generation membranes for diverse and challenging separation applications.

2:00pm **EM-TuA-3 Dry Developing Process of Molecular Layer Deposited Hf-Based Hybrid Thin Films for EUV Lithography***, Minki Choe,* ***Dan N. Le,*** *Thi Thu Huong Chu, Hyunah Sung,* University of Texas at Dallas*; Nikhil Tiwale,* Brookhaven National Laboratory*; In-Hwan Baek, Rino Choi,* Inha University, Republic of Korea*; Chang-Yong Nam,* Brookhaven National Laboratory*; Jiyoung Kim,* University of Texas at Dallas

EUVL plays a critical role in device down-scaling and thereby extending the life of Moore's law to beyond sub-7nm node. However, the current EUV photoresists based on spin-on processing and followed by wet development, which faces challenges such as high processing costs of organic solvents, pattern collapse due to capillary forces during wet development, and undercut. [1,2] These problems increase overall process costs and limit the patterning performance. In this context, fully dry lithography process has the potential to overcome the drawbacks of wet lithography and accelerate the advancement of EUV lithography.

Herein, we report a Hf-based hybrid resist thin film system that synthesized via molecular layer deposition (MLD) using Tetrakis(dimethylamido)hafnium (TDMA-Hf) and 2,3-Dimercapto-1-propanol (DMP). In our other study, we found that the Hf-based resist thin film system exhibited negative-tone behavior and excellent sensitivity, with pattern formation observed at a remarkably low dose of ~96 μC/cm^2 under 100 eV e-beam exposure. In this study, we specifically focus on investigating the dry development process using inductively coupled plasma reactive ion etching (ICP RIE) that suitable for the deposited Hf-based resist thin films. To mitigate the contribution of fluorinated greenhouse gases (F-gases) to global warming, we employed fluorine-free gases. During the etching process with fluorine-free gas, we conducted parameter optimization by varying crucial factors such as bias power, substrate temperature, and working pressure. This optimization aimed to find optimal conditions that maximize the etch rate difference between exposed and non-exposed regions. This research focuses on developing a fully dry lithography approach by combining MLD-deposited organic-inorganic hybrid photoresists with a dry development process using fluorine-free gas in ICP RIE. The goal is to establish a cost-effective and environmentally friendly lithography technique that can facilitate the realization of high-resolution patterns in EUV lithography while overcoming the limitations associated with conventional wet processes.

This work is supported by the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. Minki Choe supported by KIAT/MOTIE (RS-2024-00435406).

[1] IRDS., "Lithography & Patterning: The International Roadmap for Devices and Systems", IEEE, 1-13 (2023).

[2] Marsella, J. A., et al., "Handbook of Cleaning for Semiconductor Manufacturing",Scrivener Publishing LLC ,565-584 (2010).

2:15pm **EM-TuA-4 ALD Young Investigator Award Finalist: Inverted Living Molecular Layer Deposition: Rapid Conformal Polymer Coatings through Vapor-Phase Living Polymerization***, **Karina Ashurbekova,** Mato Knez,* CIC nanoGUNE, Spain

This study presents an inverted living MLD technique that enables precise polymer growth with tailored architectures, functional groups, and customizable properties. We present the first vapor-phase synthesis of polyoxazolines (POx) via a living cationic ring-opening polymerization (CROP) mechanism.

The two-step process involves a pulsed delivery of vaporized initiator (P-Toluenesulfonyl chloride) into a reactor, where it adsorbs onto the substrate as a molecular layer, functionalizing it. This is followed by chain propagation, where the monomer is introduced and reacts with the chemisorbed initiator layer.

We utilized three substituted oxazolines as monomers: 2-methyl-2-oxazoline, 2-phenyl-2-oxazoline, and 2-isopropenyl-2-oxazoline. The substrate was exposed to the monomer vapors for several seconds, after which the chamber was purged, and another dose of vaporized monomer was introduced. With each pulse of monomer, the polymer layer thickness gradually increased until the monomer was consumed. This allows precise control over the final coating thickness through the monomer dose and the number of feeding cycles, while still maintaining conformality of the coating. The growth process is terminated by introducing water vapor into the reactor.

The living nature of the polymerization has been confirmed by in situ QCM studies. We observed fascinating surface effects, while the composition and morphology of the POxs were examined using ATR-FTIR, XPS, SEM/TEM, and AFM. In this presentation, we focus solely on the growth of POx homopolymers, though copolymerization through sequential monomer addition is also achievable.

The key advantages of this approach include the elimination of multicomponent solution-based impurities, precise thickness control, conformality, and strong adhesion of the polymer films to a wide range of substrates.

Our approach opens the door for customization of materials for plentiful applications. As such, this development marks the beginning of a novel approach to rapid surface functionalization with highly conformal coatings with functional polymeric materials.

2:30pm **EM-TuA-5 ALD Outstanding Presentation Award Finalist: Recent Advancement of Inorganic-Organic Hybrid Resist Thin Films Deposited via Molecular Atomic Layer Deposition for Dry EUV Resist Platforms***, Dan N. Le, Thi Thu Huong Chu, Hyunah Daniela Sung, Minki Choe, Minjong Lee,* University of Texas at Dallas*; Won-Il Lee,* Stony Brook University*; Nikhil Tiwale,* Brookhaven National Laboratory*; Jean-Francois Veyan, Doo San Kim,* University of Texas at Dallas*; Chang-Yong Nam,* Brookhaven National Laboratory*;* ***Jiyoung Kim,*** University of Texas at Dallas

In order to sustain the device down scaling below the sub-1nm node, the implementation of high/hyper numerical aperture (NA) extreme ultraviolet (EUV) lithography is essential. This advancement drives the need for innovative resist platforms that meet rigorous performance criteria, including ultra-thin film (<15 nm), uniformity, mechanical and chemical robustness, and superior etch resistance. Conventional polymer-based spin-coated resists struggle to meet these stringent requirements. In contrast, ALD-based synthesized inorganic-organic hybrid dry resist thin films offer significant advantages, providing precise atomic-scale thickness control, enhanced material uniformity, and strategic incorporation of metal elements to improve sensitivity, mechanical strength, and etch resistance.

Herein, we report various molecular-atomic layer deposited hybrid resist thin film systems, contributing to the advancement of the dry EUV resist platform. We explore different combinations of metal ALD precursors, such as TMA, DEZ, TDMA-Hf with organic sources like hydroquinone (HQ), 4-mercaptophenol (4MP), and 2,3-Dimercapto-1-propanol (DMP). By using various combinations of these inorganic and organic sources, we achieve hybrid thin film systems consisting of Al-HQ, Zn-HQ, Al-4MP, Zn-4MP, Hf-

4MP, Hf-DMP, and Zn-DMP. The growth characteristics of these hybrid resist thin films were thoroughly evaluated, along with detailed material characterization. The electron sensitivity of various hybrid resist thin films was investigated using electron beam lithography (EBL) at 100 V acceleration voltage, mimicking EUV exposure conditions. Upon electron irradiation, all these hybrid resist thin film systems exhibited negative tone resist characteristics when evaluated in different developer solutions. Among these resist thin films, the Hf-DMP system demonstrated the highest sensitivity when subjected to 100 eV electron energy irradiation, requiring the lowest exposure dose to maintain most of their thickness. The chemical transformations in these hybrid resists are also investigated using *in-situ* IR spectroscopy equipped with an electron gun and a residual gas analyzer (RGA). The IR absorbance and operando RGA spectra suggested that aromatic and chain organic moieties exhibited different crosslinking pathways. Detailed experimental procedures and results will be discussed including actual EUV sensitivity of hybrid dry PRs.

This work is supported by the U.S. DOE (2023-BNL-NC033-Fund), and NRT/MSIT (2022M3H4A3052556) in Korea. We acknowledge Drs. Sangsul Lee, Geonhwa Kim, Jiho Kim at Pohang Accelerator Lab (PAL) for EUV exposure test.

2:45pm **EM-TuA-6 ALD Young Investigator Award Finalist: Rethinking Thermoelectrics: The „Power" of Hybrids Engineered by Vapor Phase Infiltration***, **Kristina Ashurbekova**,* CIC nanoGUNE, Spain*; Maksim Naumochkin, Heiko Reith, Kornelius Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany*; Mato Knez,* CIC nanoGUNE, Spain **INVITED**

Hybrid thermoelectric (TE) materials aim to outperform traditional TEs by creating synergies between organic and inorganic materials. The simultaneous exploitation of the low thermal conductivity (λ) of organics and the high Seebeck coefficient (S) and electrical conductivity (σ) of inorganics is particularly attractive. To achieve this, we developed a new family of hybrid TE materials by applying vapor phase infiltration (VPI) of Sb_2Te_3, Bi_2Te_3, Sb_2Se_3, or Bi_2Se_3 into polymeric matrices. The resulting hybrid materials feature a unique structure, with chalcogenide nanocrystals grown within the bulk of the conducting polymers.To fully understand the complexity of these hybrid materials, we extensively characterized the infiltrated chalcogenides. We observed a clear correlation between the polymer thickness and the precursor exposure time with the evolving chalcogenide crystals size within the final hybrid material. Thinner polymers resulted in smaller crystals, likely related to the faster out-diffusion of unbound precursors from the polymer during the process. TEM was used to investigate the structural organization of the nano clusters in the hybrids and to study the nucleation processes of chalcogenide nanocrystals, distinguishing between those chemically bound to the polymer chains and those physically entrapped within the polymer. SEM tomography was used to evaluate a network of chalcogenide nanocrystals inside the polymer matrix and the degree of their three-dimensional connectivity. The TE properties of the hybrids were characterized between 293–433 *K* using a lab-on-chip ZT test platform, which allowed simultaneous characterization of all in-plane parameters of the films, including the σ, *S*, λ, Hall coefficient R_H, and the derived Power Factor (PF) and ZT. Interestingly, all the measured parameters (*σ, S,* Hall coefficient R_H, λ) changed considerably within the first several heating-cooling cycles. For example, in the case of Sb_2Te_3-infiltrated PEDOT:PSS, the difference in σ between successive measurements increased to values of exceeding 80 S cm^{-1}, while the change in λ decreased. This decoupling of σ from λ is attributed to suppression of the lattice λ by enhanced boundary-scattering of heat-carrying phonons. Simultaneously, the chemical bonds between the inorganic and organic phases promote direct electronic interaction, facilitating electron transport. Finally, remarkable PF and ZT values of were obtained. This presentation will provide an overview over the conceptualization, fabrication, and evaluation of this new hybrid TE materials system, highlighting its advantage over traditional TE material concepts.

3:15pm **EM-TuA-8 Plasma-Pretreated ALD Growth of Platinum Catalysts on Carbon Nanotubes for Polymer Electrolyte Membrane Fuel Cell Applications***, **Junmo Koo**,* Korea Maritime and Ocean University, Republic of Korea*; Joon Hyung Shim,* Korea University, Republic of Korea

Platinum (Pt) catalysts are essential for polymer electrolyte membrane fuel cells (PEMFCs), but their high-cost limits commercialization. Atomic layer deposition (ALD) provides precise control over Pt catalyst growth, optimizing efficiency and stability. This study explores the impact of oxygen plasma pretreatment on Pt ALD growth on carbon nanotube (CNT) supports. Without plasma treatment, Pt formed uniformly as small nanoparticles, whereas plasma-treated CNTs exhibited sparsely distributed larger Pt clusters due to preferential nucleation sites. Electrochemical testing revealed that catalysts grown on plasma-treated CNTs exhibited higher electrochemical surface area (ECSA) and improved fuel cell performance. The larger, well-distributed Pt particles enhanced charge transfer and oxygen reduction reaction (ORR) efficiency, leading to more stable and higher power generation compared to bare CNT-supported catalysts. Our findings demonstrate that oxygen plasma pretreatment effectively modulates Pt nucleation during ALD, improving catalyst utilization and durability. This approach provides a scalable and efficient route for optimizing Pt catalyst deposition in next-generation fuel cells.

Author Index

Bold page numbers indicate presenter