

## Emerging Materials

### Room Evergreen Ballroom & Foyer - Session EM-MoP

#### Emerging Materials Poster Session

**EM-MoP-1 Conformal ALD of Ferromagnetic  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> Thin Films**, *T. Jussila*, Aalto University, Finland; *Anish Philip*, *J. Kinnunen*, *M. Utriainen*, Chipmetrics Oy, Finland; *M. Karppinen*, Aalto University, Finland

Magnetic and multiferroic thin films are vital for next-generation electronic and spintronic devices. For instance, strong room-temperature ferromagnets are required for high-density magnetic data storage while multiferroic materials could enable ultra-fast electrical writing and non-destructive magnetic reading of memory devices. However, the state-of-the-art magnetic and multiferroic materials typically have complex chemical composition including critical elements and their functional properties do not meet the requirements of the next-generation applications. Fortunately, there is a highly promising material,  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>, which possess a unique combination of multiferroic properties including ultra-hard room-temperature ferromagnetism and magnetoelectric coupling of the ferromagnetic and ferroelectric properties.<sup>[1]</sup> Moreover, this simple iron oxide is composed of Earth-abundant, low cost, and biocompatible elements. The only drawback is metastability of the  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> polymorph; it is easily transformed to more stable  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> polymorphs. Therefore, the synthesis of phase-pure  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> has been notoriously challenging which has hindered its potential for practical applications. Excitingly, atomic layer deposition (ALD) has turned out to be superiorly suited for the deposition of in-situ crystalline and amazingly stable  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> thin films from simple precursors (FeCl<sub>3</sub> and H<sub>2</sub>O) in the temperature range of 260 – 300 °C.<sup>[2]</sup> Here we show the high quality of our ALD-grown  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> thin films through <sup>57</sup>Fe Mössbauer spectroscopy, magnetic and crystallographic analyses.<sup>[3]</sup> Then, most inspiringly, we demonstrate excellent suitability of the robust  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> ALD process for high-aspect ratio substrates using PillarHall LHAR4 structures.<sup>[4]</sup> The conformality is shown using various methods such as optical microscopy, SEM, and Line scan optical reflectometry. Deposition of  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> over complex surfaces creates exciting possibilities in terms of nanostructuring (magnetic 3D nanodevices) and modification of the fine magnetic properties through dimensional effects.

#### References

- [1] J. Tuček, R. Zbořil, A. Namai, and S.-i. Ohkoshi, *Chem. Mater.* 22, 6483 (2010).
- [2] A. Tanskanen, O. Mustonen, and  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> thin films M. Karppinen, *APL Mater.* 5, 056104 (2017).
- [3] T. Jussila, A. Philip, J. Lindén, and M. Karppinen, *Adv. Eng. Mater.* 2201262 (2022).
- [4] J. Yim, O. M. E. Ylivaara, M. Ylilampi, V. Korpelainen, E. Haimi, E. Verkama, M. Utriainen, and R. L. Puurunen, *Phys. Chem. Chem. Phys.*, 22, 23107 (2020).

**EM-MoP-3 In-situ FTIR Analysis of Molecular Atomic Layer Deposited Hybrid Thin Films for EUV Resist Applications**, *Dan Le*, *S. Hwang*, *J. Veyan*, *T. Park*, *J. Kim*, University of Texas at Dallas; *R. Choi*, Inha University, Republic of Korea; *W. Lee*, *A. Subramanian*, Stony Brook University; *N. Tiwale*, *C. Nam*, Brookhaven National Laboratory; *J. Kim*, University of Texas at Dallas

The progression of lithography technology has enabled the downscaling of device feature size, prolonging Moore's law over decades. However, this has also necessitated the development of novel photoresist systems to keep pace with advancements in patterning technology. Thus, the lack of appropriate photoresist materials for EUV ( $\lambda=13.5$  nm) lithography is still a pressing challenge in the current race toward the 1 nm node. In recent years, molecular atomic layer deposition (MALD) has emerged as an innovative route to synthesize highly homogenous hybrid inorganic-organic photoresist systems with the ability to control the material thickness at the atomic-scaled level. However, as these photoresist systems have only recently been proposed, there is a gap in our fundamental understanding of the chemical reactions induced by EUV exposure.

Herein, we demonstrate a unique methodology to examine the chemical reactions that occur within MALD inorganic-organic hybrid thin films composed of trimethylaluminum (TMA) and hydroquinone (HQ) under EUV-like exposure conditions. Specifically, we have employed an in-situ Fourier-transform infrared (FTIR) spectroscopy system equipped with an

electron flood gun to examine various crosslinking mechanisms of MALD TMA/HQ hybrid thin film. Since various reported studies suggested the generation of secondary electrons during EUV exposures,<sup>1</sup> this study focuses on the interaction between electrons with energy  $\leq 80$  eV and the hybrid thin films. In addition, a residual gas analyzer (RGA) was also used to monitor the byproducts produced during the low-energy electron exposures. The obtained RGA and IR absorbance spectra revealed the role of low energy electrons in the crosslinking mechanisms responsible for the solubility switching of the MALD TMA/HQ hybrid thin films in the developer solution. Furthermore, we also studied the effects of thermal annealing on the MALD hybrid thin films before and after low-energy electron exposures. While pre-exposure baking showed no effectiveness, the post-exposure baking process demonstrated an improvement in pattern quality in terms of thickness contrast as well as edge roughness. The detailed experimental procedure and results will be discussed.

This work is supported by the GRC-NMP program (task# 3035.001) through SRC.

[1] I. Bespalov et al., *ACS Appl. Mater. Interfaces* 12, 9881 (2020).

**EM-MoP-4 Exploring the Benefits of Reduced Cycle Time in Molecular Layer Deposition (MLD) of Metal-linked 7-(trioxysilyl)heptanoate (M-TOSH)**, *Jesse Kalliomäki*, *J. Binte Mariam*, *R. Ritasalo*, *T. Sarnet*, Applied Materials, Finland

Molecular layer deposition (MLD) is being increasingly adopted by industries, like organic electronic manufacturing and medical technology. Increased interest is driven by the versatility MLD adds to the more established sister technique, Atomic Layer Deposition (ALD). Similarly with ALD, after the adoption to industrial process flow, effort must shift to increase its performance, which is measured with metrics such as throughput (wafers per hour). The principal way to increase throughput in the atomic layer processing family is to either increase the growth per cycle (GPC) or decrease cycle time. For high-GPC MLD processes, such as M-TOSH, decreasing the cycle time is an obvious low hanging fruit.

For the M-TOSH process, the literature values for cycle times in a research environment ranges from in excess of one minute [1] up to 416 s (7min) [2]. Our previously reported values in batch ALD chamber were 205 s [3]. For this work, we have studied the effect of cycle time optimization on different varieties of M-TOSH (Al, Hf, Ti) films deposited in Picosun R&P-series tools on 200 mm wafers at 90°C. The impact of decreased cycle time was studied using a range of measurement tools, including XPS, FTIR, DSA, ellipsometer.

As a result, we found out that several key process steps could be decreased by >95%. Specifically in the case of O<sub>3</sub>, reduction was found to be beneficial. Overexposure to the oxidant lead to decreased C-content, lower GPC and compromised moisture barrier properties. By adopting the reduced cycle time, M-TOSH growth rate (Å/min) was increased more than 200% and uniformity (1 $\sigma$  WiW) improved by almost 50%

This work aims to strengthen the general perception of MLD as an industrially viable deposition method and signal MLD's graduation from a research to a useful tightly optimized nanostructure engineering tool beside putting it more closely on par with other thin film deposition methods.

#### References

- [1] B.H. Lee et al. *J. Am. Soc.* 2007, 129, 51, 16034–16041
- [2] J. Huang et al. *Chem. Vap. Deposition*, 2013, 19, 142–148
- [3] Kalliomäki et al. ALD2022 conf. In Ghent, AM1-TuA-4

**EM-MoP-5 Low-Temperature Atomic Layer Annealing Deposition of Crystallized Gallium Nitride on Oxide-Free Si (111)**, *SeongUk Yun*, *A. Kummel*, *P. Lee*, *A. McLeod*, *J. Fammels*, *J. Watson*, *H. Kashyap*, University of California at San Diego; *J. Spiegelman*, RASIRC; *W. Aigner*, *T. Metzger*, Qualcomm Germany RFFE GmbH, Germany

Gallium nitride (GaN) has gained interest due to its wide band gap 3.39 eV and as a buffer layer for other III-V deposition with applications in power electronics operated at high voltage and high temperature [1]. Ueda et al. and Shih et al. showed that atomic layer annealing (ALA) improved the crystallinity of the epitaxy layers of III-V compounds (aluminum nitride) at low temperatures as compared to the conventional thermal ALD [3,4]. Rouf et al. reported that the ionized NH<sub>3</sub> or N<sub>2</sub> could deposit GaN epitaxial layers

# Monday Evening, July 24, 2023

below 250°C by using typical plasma-enhanced ALD [5]. 100 nm of SiO<sub>2</sub> and sapphire substrates were reported to deposit the crystallized GaN ALA films using krypton by UCSD. However, crystallized GaN ALA films have not been widely studied to deposit on inert, oxide-free Si (111) due to the lattice mismatch (~16%) and coefficient of thermal expansion mismatch (~54 %) between Si and GaN [2].

Thermal ALD and ALA processes were investigated for the low-temperature GaN ALD films on oxide-free Si (111). The native Si oxide was removed by dipping in 2 wt.% HF solution. The self-limiting ALD growth was achieved at 800 ms of N<sub>2</sub>H<sub>4</sub> (Rasirc), 100 ms of TDMAGa (EMD), and 400°C (Figure 1a-c). However, a significant CVD process was observed at 150 ms of TDMGa and 430°C. Lower O contents (below 3.3 at.%) were observed in four GaN ALA films on Si (111) as compared to the GaN thermal ALD film (4.6 at.%) (Fig 2a). The higher N/Ga atomic ratio in the GaN ALA films than those in the thermal ALD suggested the ALA process improved the quality of GaN thin films. It is noted the low N/Ga ratio is an artifact of the AES sensitivity factors and ex-situ XPS confirmed a nearly stoichiometric N/Ga ratio.

The intensity of GaN (200) XRD pattern in GaN ALD films on Si was increased with the pulse length of Ar plasma up to 15-20 s (Figure 2b), suggesting the ALA process could improve the crystallinity of GaN epilayers. The excess ALA plasma (30 s) could damage the crystallized GaN epilayers. Smooth surface morphologies were observed in the GaN ALD films (RMS = 0.6~1.0 nm) regardless of Ar plasma pulse length (not shown). The Ga-N species in both spectra of Ga 2p<sub>3/2</sub> (Figure 3a) and N 1s (Figure 3b) were dominant after 10 min Ar sputtering and oxide species disappeared after 20 min Ar sputtering, suggesting the formation of good-quality GaN film without Ga-O bonds. These observations suggested that high-quality crystallized GaN ALD thin films with a smooth surface were successfully deposited on oxide-free Si (111) using 15 s of the ALA process at a low temperature (275°C) using TDMAGa and N<sub>2</sub>H<sub>4</sub> precursors.

## EM-MoP-6 Vapor Deposited MOFs as Low-K Dielectrics for Logic and RF, J. Watson, Dohyun Go, A. Kummel, UCSD

The present work investigates metal-organic frameworks (MOFs) as low-k dielectrics used to fill the gaps between vias or interconnects in the semidamascene process. An ALD grown ZnO layer is converted to the MOF ZIF-8 by dosing the ZnO in an organic linker gas at elevated temperature. The present study determined the key factors in maximizing the 12x volumetric expansion which is critical to gap fill: The volumetric expansion is a function of the crystallinity of the ZnO film, which depends on the substrate temperature of the ALD process. Three different MOF reaction processes were compared: sealed isothermal, sealed temperature differential, and unsealed temperature differential which were all in atmosphere. The sealed isothermal method provided materials at least as good as the more complex methods.

Three substrate temperatures for the ALD ZnO process were examined to investigate the effect on crystallinity of the ZnO film and subsequent MOF layer thickness. XRD measurements demonstrate that crystallinity decreases with decreasing ALD temperature (Fig 1a). These films were converted to MOF using the same sealed isothermal process. The volumetric expansions as determined by ellipsometry for the three films in order of lowest to highest ALD temperature was 11.2x, 7.5x, and 7.7x (Fig 1b). It is concluded that low-temperature deposited ZnO has higher MOF conversion due to lower crystallinity.

Incorporating a temperature differential into the MOF conversion reaction with a sealed container resulted in the build-up of organic linker vapor near the cold substrate which caused organic linker crystals to condense on the ZnO. Shown in Figure 2, incorporating the temperature differential with an unsealed container showed equivalent results to that of the sealed isothermal container, with roughly 12.2x conversion after two hours. Since the unsealed temperature differential set-up is less reproducible, it is concluded that running the MOF reaction isothermally in sealed conditions is superior. Running the MOF reaction under vacuum will be investigated. It is also noted that the RMS roughness of the initial ZnO layer was roughly 6% of the ZnO thickness, while the MOF layer's RMS roughness was roughly 20% of the MOF layer thickness. Finally, to demonstrate the gap filling ability of the MOF conversion process, the 0 nm 4patterned trenches will be filled which have a 5:1 aspect ratio (Fig 3).

## EM-MoP-8 Towards Sequentially Infiltrated Two-Photon Polymerized 3D Photonic Crystals for Mid-IR Spectroscopic Applications, A. Singhal, University of Illinois - Chicago; Ralu Divan, Argonne National Laboratory; A. Dalmiya, P. Lynch, University of Illinois - Chicago; L. Stan, Argonne National Laboratory; I. Paprotny, University of Illinois - Chicago

Photonic crystals (PhCs) can slow the group velocity of light for enhanced light-matter interaction, enabling applications in mid-infrared (MIR) spectroscopic sensing systems [1]. The photonic bandgap (PBG) is a group of wavelengths that are forbidden to pass through the PhCs. Over planar microfabrication techniques, two-photon polymerization (2PP) allows rapid fabrication of 3D-PhCs. But 2PP materials have a low refractive index, which leads to only partial PBGs. The process of sequential infiltration synthesis (SIS), derived from atomic layer deposition (ALD) [2], allows precursor gases to infiltrate and react deep within the polymer [3], resulting in increased refractive index.

In this work, we present 2PP-fabricated IP-Dip resin-based 3D PhCs and use SIS to achieve broad PBG. The partial PBG was confirmed by Fourier transform infrared spectroscopy (FTIR) analysis. For infiltration testing, 100 μm cubes were fabricated at a 700 nm hatching distance and ZnO SIS was performed. The ZnO-infiltrated cube was focused ion beam (FIB) half-milled, and energy dispersive spectroscopy (EDS) was performed on the milled structure, showing counts of Zn L-shell, confirming infiltration. SIS is further used on 2PP-fabricated PhCs to achieve increased refractive index, making PhCs suitable for applications in MIR spectroscopic sensing.

[1] Singhal, A. et al (2022) IEEE Sensors J. 22-21, 20126-20137

[2] Peng, Q. et al (2011) ACS Nano, 5-6, 4600-4606

[3] Ramanathan, M. et al (2013) J. Mater. Chem. 1-11, 2080-2091

Part of the work performed at the Center for Nanoscale Materials, a U.S. Department of Energy

Office of Science User Facility, was supported by the U.S. DOE, Office of Basic Energy Sciences,

under Contract No. DE-AC02-06CH11357.

## Emerging Materials

### Room Regency Ballroom A-C - Session EM-WeM

#### EUV Litho Materials

Moderator: Ms. Haripin Chandra, EMD Electronics, USA

#### 10:45am EM-WeM-12 Novel Organic-Inorganic Hybrid Thin Films Deposited by Molecular Atomic Layer Deposition (MALD) for EUV Resist Applications, *Jiyoung Kim*, University of Texas at Dallas **INVITED**

Continued extreme downscaling of semiconductor devices and their high-volume manufacturing hinge on EUV lithography ( $\lambda=13.5$  nm, EUVL), especially the soon-planned implementation of high numerical aperture (NA) EUVL. Photoresist (PR) materials are a crucial area that demands significant improvement for the high NA EUVL, particularly in achieving ultrathin thickness, uniform composition and high patterning performance (e.g., EUV sensitivity, pattern resolution, critical dimension uniformity), as well as increased etch resistance.

In this talk, we will introduce an innovative synthesis route for organic-inorganic hybrid photoresists, which leverages the molecular atomic layer deposition (MALD) of ultrathin films comprised of organic and inorganic components. Specifically, we will discuss the fabrication of a hybrid resist system, which is composed of trimethylaluminum (TMA) and hydroquinone (HQ), and its characteristics under exposure using a low energy electron beam to mimic expensive and rare EUV lithography. Most importantly, we will focus on the low-energy electron exposure characteristics, investigated using an *in-situ* infrared spectroscopy system. The TMA-HQ hybrid resists not only exhibited a comparable 100 kV EBL performance to that of HSO (hydrogen silsesquioxane), a commercial negative-tone EBL resist but also sustained the negative tone under low-energy electron exposures down to  $\sim 100$  eV and lower electron energy (evaluated in diluted AZ 300 MIF solution). Furthermore, the dose-dependent characteristics of the MALD hybrid resists were also investigated at various low electron energies via EBL and electron flood gun system. The post-development remaining thickness of the exposure dose matrices was determined using atomic force microscopy (AFM), in which the required dose to maintain 50% of resist thickness (critical dose) was estimated to be approximately  $8.4$  mC/cm<sup>2</sup> at 100 eV. The obtained *in-situ* IR absorbance spectra suggested that chemical reactions involving aromatic rings of HQ as well as the reduction of C–O bonding are contributed to the formation of a crosslinking network within the TMA-HQ hybrid resist. We will also briefly go over the dry etching characteristics of the resist, identifying a potential process window for dry development.

This study is supported by the GRC-NMP program (task# 3035.001) through SRC.

#### 11:15am EM-WeM-14 Inorganic Cluster Synthesis and Characterization via Atomically Precise ALD in Polymers, *T. Kunene, Alex Martinson*, Argonne National Laboratory

Precision inorganic clusters, with atom-count between single-atom-sites and nanoparticles, offer an enticing complement of atom-efficiency, unique composition and structure that may defy bulk extended solids, and a total atom count that allows affordable first-principles computation of structure-function relationships. In previous work we demonstrated a novel route to few-atom inorganic cluster synthesis in a polymer matrix [ACS Nano 2020, 14, 11, 14846–14860] through sequential infiltration synthesis (SIS) of inorganic solids in analogy to atomic layer deposition (ALD) but that occurs within (vs upon) a soft material template. Careful control of synthesis conditions affords few-atom clusters of indium oxyhydroxide with relatively uniform structure. In more recent work, we probe the unique optical and vibrational properties of these small InO<sub>x</sub>Hy clusters and begin to consider their potential for CO<sub>2</sub> capture and conversion. We describe a refinement of the SIS process that favors the formation of new clusters in the first cycle, while favoring cluster growth only in subsequent cycles. This approach affords more uniform cluster growth with characteristic vibrational spectra as acquired with *in situ* infrared spectroscopy. Spectral analysis provides insight into cluster size and chemical functionality that evolves with additional SIS cycles (i.e. cluster growth). Optical absorption spectroscopy further reveals the unique and size-dependent properties of the few-atom clusters relative to bulk phases. Gentle thermal treatment of the polymer-embedded clusters provides the first insight into SIS-derived cluster stability, which exceeds 200 °C.

#### 11:30am EM-WeM-15 Molecular Layer Deposition of Al- and Hf-Based Hybrid Resists for Electron-Beam and EUV Lithography, *A. Ravi, J. Shi, J. Lewis, Stacey Bent*, Stanford University

The development of new resist materials is required to enable extreme ultraviolet (EUV) lithography for next-generation microelectronics. Inorganic resists are a promising class of materials because compared to traditional organic resists, they have higher etch resistance, are more impervious to pattern collapse, and are more absorbing of EUV radiation. However, there is limited understanding about how they behave under irradiation as well as what chemical and structural properties of the resist are most beneficial. In this work, we study the molecular layer deposition (MLD) of Hf- and Al-based hybrid thin film resists, known as “hafnicone” and “alucone.” These materials are grown at 100 °C using the metal precursors tetrakis(dimethylamido)hafnium(IV) and trimethylaluminum together with ethylene glycol as the organic counterreactant. Both alucone and hafnicone are tested against electron beam exposure to inform their behavior under EUV, and results show that they behave as negative tone resists. Hafnicone exhibits a sensitivity of 400  $\mu\text{C}/\text{cm}^2$  and the ability to resolve 50 nm line widths. Alucone’s line patterns are more sharply defined than those of hafnicone, suggesting higher resolution. However, whereas alucone’s sensitivity is 4800  $\mu\text{C}/\text{cm}^2$  using 0.125 M HCl as the developer, hafnicone’s sensitivity is 400  $\mu\text{C}/\text{cm}^2$  using 3 M HCl. The MLD resists are additionally characterized via X-ray photoelectron and infrared spectroscopy to investigate the patterning mechanism, which is described in the context of classical nucleation theory. This study of hafnicone and alucone hybrid MLD offers new insight into structural features of an MLD film that can lead to desired EUV-responsive behavior. This insight may accelerate the development of vapor-deposited inorganic resists for use in electron-beam and EUV lithography.

#### 11:45am EM-WeM-16 High-resolution EUV Lithographic Patterning Characteristics of InO<sub>x</sub>-PMMA Hybrid Photoresist Generated by Vapor-phase Infiltration, *A. Subramanian*, Stony Brook University; *N. Tiwale*, Brookhaven National Laboratory; *W. Lee*, Stony Brook University; *K. Kissinger*, *M. Lu*, *A. Stein*, Brookhaven National Laboratory; *J. Kim*, University of Texas at Dallas; *Chang-Yong Nam*, Brookhaven National Laboratory/Stony Brook University

Continuing extreme downscaling of semiconductor devices is essential for high performance and energy efficiency of the current and future microelectronics. Adoption of extreme ultraviolet lithography (EUVL) is poised to drive the device miniaturization into the angstrom era in near future. However, there are several material-related challenges in EUVL, and one of them is the need for developing improved EUV photoresists that can feature simultaneously high sensitivity, resolution, and etch selectivity. One strategy being explored in the field is to synthesize inorganic-containing hybrid resists that utilize high EUV sensitivity and etch resistance of inorganic elements. However, currently available hybrid EUV photoresists are mostly chemically synthesized, requiring complex and slow development and processing steps for production or modification of resist properties, while suffering from a short shelf-life. Additionally, most of the reported systems are negative-tone, crosslinking resists, which are capable of patterning line gratings or pillars but require multiple exposures or complex processing for contact-hole patterning in memory devices. In this work, we demonstrate a new, positive-tone, organic-inorganic hybrid EUV resist that delivers the high-resolution EUVL and electron-beam lithography (EBL) patterning capability combined with high etch resistance and Si etch selectivity. The new resist, poly(methyl methacrylate) infiltrated with indium oxide (PMMA-InO<sub>x</sub>), is generated via vapor-phase infiltration (VPI)—a gaseous material hybridization technique derived from atomic layer deposition (ALD). The weak binding nature of the gaseous indium precursor, trimethylindium (TMIn), to the carbonyl group in PMMA allows the synthesis of hybrids with inorganic content distributed uniformly across the thickness of the resist. The new hybrid resist achieves: (a) high EUVL and EBL sensitivities as low as 18 mJ/cm<sup>2</sup> and 300  $\mu\text{C}/\text{cm}^2$ , respectively, (b) high-resolution positive-tone EUVL patterning capability (e.g., 40 nm half-pitch line-space and 50 nm diameter contact hole patterns), and (c) high Si etch selectivity (>30 – 40), when combined with optimized pre- and post-patterning resist process strategies comprising underlayer application and post-development descum procedures for addressing InO<sub>x</sub> residues. The results not only hint at the potential of VPI-based ex-situ hybridization in developing novel hybrid EUV photoresists but also can pave the way for using infiltration-synthesized hybrid thin films as reliable positive-tone EUVL photoresists without chemical amplification.

## Emerging Materials

### Room Regency Ballroom A-C - Session EM1-WeA

#### Molecular Layer Deposition

**Moderator:** Prof. Dr. Jiyoung Kim, University of Texas at Dallas

1:30pm **EM1-WeA-1 MLD/ALD of Hybrid Dielectrics for Flexible Electronic Devices**, *X. Wang*, School of Advanced Materials, Shenzhen Graduate School, Peking University, China; *Min Zhang*, School of Electronic and Computer Engineering, Shenzhen Graduate School, Peking University, China

#### INVITED

Modern information technologies have tremendous demands on flexible electronic devices such as thin-film transistors (TFTs). As the flexible TFT technology continues to advance, the properties of the gate dielectric become a bottleneck for the flexible TFTs to achieve fast switching speed, low operation voltage, and downscaling. The gate dielectric layer should be sufficiently thin, insulating, and flexible, and therefore, hybrid organic-inorganic dielectrics are of great promise for this purpose. In this work, we develop an MLD/ALD technique to grow a hybrid material of polyimide and Al<sub>2</sub>O<sub>3</sub> (HPA) and show that the afforded HPA films are well suited as the bendable gate dielectrics for flexible electronic applications. The MLD/ALD growth mechanism is carefully investigated, and it is found that the growth of polyimide is strongly affected by the Al<sub>2</sub>O<sub>3</sub> surface and therefore exhibits a two-stage behavior. We further show that the HPA films can serve as a good gate dielectric to realize the intrinsic flexibility of transistors and circuits based on carbon-nanotubes (CNTs). With this hybrid dielectric, high-performance all-CNT TFTs and integrated circuits of inverters, ring oscillators, and logic gates are demonstrated. Particularly, the inverters exhibit a remarkably high gain of 342.5 and can be used as an analog amplifier for millivolt small signals. Ultralow voltage (50 mV) operation is also feasible, which highlights the great promise for low-power applications.

2:00pm **EM1-WeA-3 The Molecular Evolution of ZnO Sequential Infiltration Synthesis**, *I. Weisbord*, *M. Barzilay*, Department of Chemical Engineering, Technion, Israel; *A. Kuzmin*, *A. Anspoks*, Institute of Solid State Physics, University of Latvia; *E. Welter*, Deutsches Elektronen-Synchrotron, Germany; *Tamar Segal-Peretz*, Department of Chemical Engineering, Technion, Israel

Sequential infiltration synthesis (SIS) has emerged in the past decade as a powerful technique for hybrid material fabrication through high-precision growth of inorganic materials within polymers using atomic layer deposition (ALD) chemistry. In SIS, ALD precursors diffuse into the polymer and interact with it, leading to inorganic materials growth within the polymer's free volume. If desired, the polymer can later be removed, yielding polymer-templated inorganic structures. Among the limited but growing list of inorganic materials demonstrated via SIS, ZnO stands out as a promising material in wide and diverse applications which can harness SIS abilities for low-cost, large-area, and high-quality nanostructure fabrication.

In this study, we have probed the development of ZnO, grown within various polymers *via* SIS. We combined high-resolution scanning transmission electron microscopy (STEM) and *in-situ* thermal TEM, together with synchrotron-based X-ray absorption near edge structures (XANES) and show, for the first time, the evolution of polycrystalline Wurtzite ZnO cluster and nanoparticles- from the onset of crystallinity after just single SIS cycle, through the cycle-by-cycle 3D growth of the particles. *In-situ* growth analysis using microgravimetry and FTIR enabled us to shed light on the growth mechanism and its deviation from classic ALD-like growth, as well as to understand the role of polymer chemistry on the growth nucleation and particle density within the polymer. Annealing the hybrid ZnO-polymer films in air removes the polymers and consolidates the as-grown clusters and nanoparticles into a network of polycrystalline ZnO particles. Our findings lay the foundations for ZnO SIS design rules and rational hybrid and inorganic nanostructures design.

2:15pm **EM1-WeA-4 Conformal ALD/MLD of Perfectly Stable Zn-Benzenedithiol Thin Films**, *T. Jussila*, Aalto University, Finland; *A. Philip*, *J. Kinnunen*, Chipmetrics Oy, Finland; *D. Zanders*, Ruhr-University Bochum, Germany; *M. Utriainen*, Chipmetrics Oy, Finland; *A. Devi*, Ruhr-University Bochum, Germany; *Maarit Karppinen*, Aalto University, Finland

The combined atomic/molecular layer deposition (ALD/MLD) technique is an ideal route for high-quality metal-organic thin films;<sup>[1]</sup> it enables well-controlled integration of the inorganic and organic components through strong chemical bonding. Moreover, these hybrid thin films can be

deposited even on high aspect ratio 3D substrates. Here we introduce a novel ALD/MLD process for amorphous, ambient air-stable Zn-BDT thin films grown from Zn(DMP)<sub>2</sub> (bis-3-(N,N-dimethylamino)propyl)<sup>[2,3]</sup> and BDT (benzene-1,4-dithiol) precursors. The film growth shows clear saturation with 3 s pulse length for both precursors and the growth-per-cycle (4.5 Å/cycle) remains nearly constant even with excessive 30 s pulsing times. Moreover, the process has a stable temperature window of at least 60 – 70 °C and the film growth is perfectly linear. Most excitingly, due to the nearly ideal ALD/MLD growth characteristics, the deposition process is well-suited for coating of high-aspect ratio surfaces; we demonstrate the excellent fitness of our Zn-BDT process for PillarHall LHAR<sup>[4]</sup> structures using excessive 30 s pulse lengths for both precursors to obtain high penetration depth without any noticeable effect on the growth rate. Composition of the amorphous films is characterized with FTIR and Raman spectroscopy while the coverage and penetration of the conformal films are analysed with optical microscopy, SEM, and Line scan optical reflectometry. This work demonstrates the excellent feasibility of the state-of-the-art ALD/MLD for high-aspect ratio surfaces.

#### References

- [1] J. Multia and M. Karppinen, *Adv. Mater. Interfaces* 9, 2200210 (2022).
- [2] L. Mai, F. Mitschker, C. Bock, A. Niesen, E. Ciftiyurek, D. Rogalla, J. Mickler, M. Erig, Z. Li, P. Awakowicz, K. Schierbaum, and A. Devi, *Small* 16, 1907506 (2020).
- [3] A. Philip, L. Mai, R. Ghiyasi, A. Devi, and M. Karppinen, *Dalton Transact.* 51, 14508 (2022).
- [4] J. Yim, O. M. E. Ylivaara, M. Ylilammi, V. Korpelainen, E. Haimi, E. Verkama, M. Utriainen, and R. L. Puurunen, *Phys. Chem. Chem. Phys.* 22, 23107 (2020).

2:30pm **EM1-WeA-5 Recent Developments in Oxidative Molecular Layer Deposition (oMLD)**, *Matthias Young*, *Q. Wyatt*, *K. Brathwaite*, *M. Ardiansyah*, *N. Paranamana*, *K. Brorsen*, University of Missouri

The first demonstration of oxidative molecular layer deposition (oMLD) was reported in 2014, forming poly(3,4 ethylenedioxythiophene) (PEDOT) using sequential self-limiting exposures of ethylenedioxythiophene (EDOT) monomers and an MoCl<sub>5</sub> chemical oxidant. In the last few years, the number of chemistries that have been demonstrated using oMLD has expanded to include at least four additional monomers, with successful demonstrations using at least three different chemical oxidants. However, limited mechanistic understanding of oMLD is impairing progress in this field. Here, we report on recent work examining the mechanisms for oMLD growth. We examine oMLD growth using EDOT, pyrrole (Py), paraphenylenediamine (PDA), thiophene (Thi), and furan (Fu) monomers. We specifically identify the importance of a two-electron chemical oxidant in these reactions, which must have sufficient oxidation strength to oxidize both a surface and a gas-phase monomer to enable oMLD growth. The mechanistic insights from these studies provides a conceptual framework to enable rational molecular assembly of copolymer structures by oMLD. Using this concept, we generate copolymer structures with improved electrochemical properties over the corresponding isolated homopolymers. The insights from this study suggest a pathway to address previously intractable questions regarding the molecular origins of polymer properties, and allowing us to control and optimize polymer structure and properties for electrochemical applications including energy storage, water desalination, and sensors.

2:45pm **EM1-WeA-6 In Situ Analysis of Growth Mechanism During Molecular Layer Deposition of Polyurea**, *Wallis E. Scholl*, Colorado School of Mines; *E. Hudson*, *L. Belau*, Lam Research Corporation; *S. Agarwal*, Colorado School of Mines

Although molecular layer deposition (MLD) has been studied for more than two decades, the mechanism of MLD film growth is not well understood. In idealized MLD, each bifunctional precursor reacts with the substrate surface through only one functional group, depositing a single monomer layer. Although previous research has shown a linear growth per cycle, the film thickness deposited per cycle is often much lower than the length of

# Wednesday Afternoon, July 26, 2023

one repeat unit of the polymer chain<sup>1</sup>. This has previously been attributed to reactive site consumption by double reactions, in which both ends of a precursor react with the surface, reducing the number of reactive sites for the next cycle. Re-nucleation of chains through precursor adsorption may account for continuation of growth after terminations reduce the number of surface sites.<sup>1,2</sup>

In this study, we used *in situ* attenuated total reflection Fourier transform infrared spectroscopy and *in situ* four-wavelength ellipsometry to monitor film composition and thickness throughout molecular layer deposition of polyurea with 1,4 diisocyanatobutane (DICB)/diethylenetriamine (DETA). Figure 1 shows the infrared absorbance change throughout the first 5 cycles of MLD. We show that the stretching mode for N=C=O functional group in DICB, which is associated with the number of reactive sites following the DICB half cycle, gradually decreased with increasing number of MLD cycles. Despite this loss of reactive sites, film growth continued even at a high number of cycles, which suggests that new site creation drives continuation of growth. This progression is supported by film thickness measured by *in situ* ellipsometry (see Figure 2); initial growth rates gradually slow down as double reactions consume reactive sites, until a steady growth rate is reached in which site consumption via double reactions and site creation via precursor adsorption is balanced. Further, we found that MLD growth is highly dependent on substrate surface preparation, which dictates the initial number of surface sites available. When initial reactive sites are below a critical density, precursor adsorption is unable to compensate and film growth remains low throughout deposition.

<sup>1</sup> Bergsman *et al.*, *Chem. Mater.*, 30, 1, 2018.

<sup>2</sup> Nye *et al.*, *Dalton Trans.*, 51, 2022.

3:00pm **EM1-WeA-7 A Chemist's Lego Blocks: Molecular Layer Deposition (MLD) for Nanoelectronic Applications**, *Michelle Paquette*, University of Missouri-Kansas City

**INVITED**

Molecular layer deposition (MLD), similarly to atomic layer deposition (ALD), consists of layer-by-layer deposition via sequential self-limiting reaction half cycles. In contrast to ALD, MLD uses as fundamental building blocks organic molecules rather than single atoms. So-called hybrid MLD processes make use of both atomic and molecular building blocks. Both ALD and MLD have risen dramatically in popularity over the last several decades due to their control over thin-film conformality as well as quality, thickness, and uniformity at the nanoscale. This talk will cover the different classes of MLD schemes and materials and their use and potential advantage in nanoelectronics, including front-end-of-the-line, back-end-of-the-line, memory, and patterning applications.

## Author Index

### Bold page numbers indicate presenter

— A —

Agarwal, S.: EM1-WeA-6, 4  
Aigner, W.: EM-MoP-5, 1  
Anspoks, A.: EM1-WeA-3, 4  
Ardiansyah, M.: EM1-WeA-5, 4

— B —

Barzilay, M.: EM1-WeA-3, 4  
Belau, L.: EM1-WeA-6, 4  
Bent, S.: EM-WeM-15, **3**  
Binte Mariam, J.: EM-MoP-4, 1  
Brathwaite, K.: EM1-WeA-5, 4  
Brosen, K.: EM1-WeA-5, 4

— C —

Choi, R.: EM-MoP-3, 1

— D —

Dalmiya, A.: EM-MoP-8, 2  
Devi, A.: EM1-WeA-4, 4  
Divan, R.: EM-MoP-8, **2**

— F —

Fammels, J.: EM-MoP-5, 1

— G —

Go, D.: EM-MoP-6, **2**

— H —

Hudson, E.: EM1-WeA-6, 4  
Hwang, S.: EM-MoP-3, 1

— J —

Jussila, T.: EM1-WeA-4, 4; EM-MoP-1, 1

— K —

Kalliomäki, J.: EM-MoP-4, **1**  
Karppinen, M.: EM1-WeA-4, **4**; EM-MoP-1, 1

Kashyap, H.: EM-MoP-5, 1

Kim, J.: EM-MoP-3, 1; EM-WeM-12, **3**; EM-WeM-16, 3

Kinnunen, J.: EM1-WeA-4, 4; EM-MoP-1, 1

Kisslinger, K.: EM-WeM-16, 3

Kummel, A.: EM-MoP-5, 1; EM-MoP-6, 2

Kunene, T.: EM-WeM-14, 3

Kuzmin, A.: EM1-WeA-3, 4

— L —

Le, D.: EM-MoP-3, **1**

Lee, P.: EM-MoP-5, 1

Lee, W.: EM-MoP-3, 1; EM-WeM-16, 3

Lewis, J.: EM-WeM-15, 3

Lu, M.: EM-WeM-16, 3

Lynch, P.: EM-MoP-8, 2

— M —

Martinson, A.: EM-WeM-14, **3**

Mcleod, A.: EM-MoP-5, 1

Metzger, T.: EM-MoP-5, 1

— N —

Nam, C.: EM-MoP-3, 1; EM-WeM-16, **3**

— P —

Paprotny, I.: EM-MoP-8, 2

Paquette, M.: EM1-WeA-7, **5**

Paranamana, N.: EM1-WeA-5, 4

Park, T.: EM-MoP-3, 1

Philip, A.: EM1-WeA-4, 4; EM-MoP-1, **1**

— R —

Ravi, A.: EM-WeM-15, 3

Ritasalo, R.: EM-MoP-4, 1

— S —

Sarnet, T.: EM-MoP-4, 1

Scholl, W.: EM1-WeA-6, **4**

Segal-Peretz, T.: EM1-WeA-3, **4**

Shi, J.: EM-WeM-15, 3

Singhal, A.: EM-MoP-8, 2

Spiegelman, J.: EM-MoP-5, 1

Stan, L.: EM-MoP-8, 2

Stein, A.: EM-WeM-16, 3

Subramanian, A.: EM-MoP-3, 1; EM-WeM-16, 3

— T —

Tiwale, N.: EM-MoP-3, 1; EM-WeM-16, 3

— U —

Utriainen, M.: EM1-WeA-4, 4; EM-MoP-1, 1

— V —

Veyan, J.: EM-MoP-3, 1

— W —

Wang, X.: EM1-WeA-1, 4

Watson, J.: EM-MoP-5, 1; EM-MoP-6, 2

Weisbord, I.: EM1-WeA-3, 4

Welter, E.: EM1-WeA-3, 4

Wyatt, Q.: EM1-WeA-5, 4

— Y —

Young, M.: EM1-WeA-5, **4**

Yun, S.: EM-MoP-5, 1

— Z —

Zanders, D.: EM1-WeA-4, 4

Zhang, M.: EM1-WeA-1, **4**