

## 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 LHAR4<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

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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.

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