Emerging Materials
Room Van Eyck - Session EM-WeM2
Molecular Layer Deposition

Moderators: Arrelaine Dameron, Forge Nano, Ola Nilsen, University of Oslo

10:45am **EM-WeM2-1 Deposition of Copper-based Metal-Organic Framework Thin Film by Molecular Layer Deposition***, **Ben Gikonyo**, C. Journet-Gautier, A. Fateeva, C. Marichy,* Université Claude Bernard Lyon 1, France

Metal-organic frameworks (MOFs) are a class of hybrid materials composed of metal ions/clusters bridged by organic moieties. They have received much attention in recent years as promising porous materials that are highly adaptable to a wide range of applications, such as gas storage or separation, catalysis, sensors, or electrochemistry. In the later field, MOFs are gaining ground for rechargeable batteries, fuel cells, or electrocatalysis. For real breakthroughs, fine-tuning of their structure and thus physico-chemical properties with remarkable precision is required. MOFs have been synthesized mainly as a powder or single crystals but to integrate these hybrid materials into microelectronics, thin films are needed.[1,2] In this regard, molecular layer deposition (MLD) appears as a technique of choice.[3]Based on sequential self-limited gas-surface reactions, it allows fabricating solvent-free films with control of the thickness at the nanoscale level. Although around ten MOFs[4-7] have been successfully grown by MLD, obtaining layers with good porosity and crystallinity remains a major challenge. Nevertheless, amorphous as-grown films have been crystallized by post-deposition treatments that involve exposing the film in a controlled condition with humidity and acetic acid/DMF vapors.[8]

Herein, the direct growth of copper-based MOFs by MLD is presented. Two frameworks are successfully deposited using a homemade reactor: Copper terephthalate (Cu-TP), even though already reported by another group**[6]**,and the porphyrinic MOF, Cu-TCPP (TCPP=meso-tetra(4-carboxyphenyl) porphyrin), attractive for its optical and redox properties. The obtained films are characterized using ellipsometry, UV-Visible, and IR spectroscopies, PXRD and SEM.

On the contrary to the pioneering work,**[6]** our *as*-deposited Cu-TP film is directly obtained crystallized into the known desolvated phase.[9]Optimum deposition condition and self-limiting property of the precursors/substrate reactions for Cu-TCPP are established. Rough films with a hybrid composition are observed. Hetero-MOF structures made of single DMOF-1 crystals coated with a homogenous Cu-based MOF layer are also reported.

1. J. E. Ellis *et al.,Mater. Adv.* 2, 6169, (2021)
2. O. Shekhah *et al.,* Chem. Soc. Rev., 40, 1081–1106 (2011)
3. C. Crivello *et al.*, *Mater. Horiz.*8, 168–178 (2021)
4. L. D. Salmi *et al.*, *Microporous and Mesoporous Mater.*182, 147–154 (2013)
5. L. D. Salmi *et al.*, *J. Vac. Sci. Technol. A*33, 01A121 (2014)
6. E. Ahvenniemi, M. Karppinen, *Chem. Commun.*52, 1139–1142 (2016)
7. E. Ahvenniemi, M. Karppinen, *Chem. Mater.*28, 6260–6265 (2016)
8. K. B. Lausund, O. Nilsen, *Nat Commun*. 7, 13578 (2016)
9. C. G. Carson *et al.*, *Eur. J. Inorg. Chem.* 2140–2145 (2014)

11:00am **EM-WeM2-2 ALD-Grown ZIF-8 Thin Films : Mechanism Insight Leads to Push Beyond the Current Thickness Limit***, V. Perrot,* Univ. Grenoble Alpes, CEA, LETI, France*; A. Roussey,* Univ. Grenoble Alpes, CEA, LITEN, France*; M. Veillerot, A. Benayad, D. Mariolle, F. Ricoul, V. Jousseaume,* Univ. Grenoble Alpes, CEA, LETI, France*; **Elsje Alessandra Quadrelli,*** CNRS, Univ Lyon IRCELYON , France

Completely vapor phase-based routes for the synthesis of Metal Organic Frameworks (MOF) are recent (see, for example, [1] and [2]). Vapour-phase processes are usually preferred to obtain conformal coatings in the high aspect ratio features of devices but much still remains to be done to control the growth and understand the potential and the limits of these growth methods.

In this work, pinhole-free and crystalline zeolitic imidazolate framework-8 (ZIF-8) layers as thick as 250 nm were grown, by integrating the method previously reported [1]- which typically levels off below 100 nm- in a novel cycling process.
Different types of substrates and devices were used, such as silicon wafers, Quartz Crystal Microbalance and silicon micro-pillars arrays, see Figure1).
The material properties as well as the impact of the process parameters on the MOF growth will be reported (data include electronic microscopy, ellipsometric-porosimetry, X-ray diffraction and a study on the influence of water pressure on the final thickness).
Molecular-level mechanistic reasons behind the current thickness bottleneck will be discussed through a ToF-SIMS and XPS profil study at different stages of growth.

[1] I. Stassen et al., *Nat. Mat.*, **15**, 304–310 (2016)

[2] E. Ahvenniemi et al., *Chem. Com.*, **52**, 1139-1142 (2016)

11:15am **EM-WeM2-3 Molecular Layer Deposition of Zeolitic Imidazolate Framework 8 Thin Films***, **Jorid Smets**, A. Cruz, R. Ameloot,* KU Leuven, Belgium

Vapor-phase thin film deposition of metal-organic frameworks (MOFs) is required to integrate these materials into electronic devices. Here, we study the molecular layer deposition (MLD) of zeolitic imidazolate framework 8 (ZIF-8), a MOF comprised of zinc nodes connected by 2-methyl imidazolate linkers. In this all-vapor-phase process, thin films are deposited by consecutive self-limiting reactions of diethyl zinc, water, and 2-methyl imidazole. We developed two different methods: (1) Direct ZIF-8 MLD employs only self-limiting reactions resulting in smooth films, crystallinity, and nanometer-scale thickness control, and (2) Two-step ZIF-8 MLD, in which the surface reaction with the linker is completed through a post-treatment step instead of during the MLD deposition. The latter approach resulted in a much faster deposition and an improved MOF quality, *i.e.,* increased crystallinity and probe molecule uptake at the expense of a higher roughness and less precise thickness control. All depositions were performed using a modified commercial ALD reactor, ensuring cleanroom compatibility. *In situ* ellipsometry was employed to monitor the MOF growth and assess the probe molecule uptake. Various *ex situ* techniques, such as atomic force microscopy and grazing incidence XRD were used to supplement the *in situ* techniques and evaluate the coating quality. The critical parameters of the ZIF-8 MLD process were identified, facilitating the adoption of MOF-MLD in other facilities.

11:30am **EM-WeM2-4 Mld of Phosphane-Ene Polymer Thin Films: Bringing Solution Polymer Chemistry to a Gas Phase Process***, J. Lomax,* The University of Western Ontario, Canada*; E. Goodwin, P. Gordon,* Carleton University, Canada*; C. McGuiness,* Solvay*; C. Crudden,* Queen's University, Canada*; S. Barry,* Carleton University, Canada*; **Paul J. Ragogna,*** The University of Western Ontario, Canada

Over the past several years, the Ragogna group has discovered and prepared bulk samples of novel photopolymers from solution via the phosphane-ene reaction, which is the addition of a P-H bond to C-C double or triple bond. These are materials rich in phosphorous content, and the bulk polymers have been used to as precursors to prepare metal-phosphide ceramics and as getters in metal sequestration applications.

Given the unique properties and well-understood reaction chemistry for phosphane-ene materials, we undertook to transfer the phosphane-ene reaction to the gas phase for the deposition of thin films (10-100 nm) via plasma enhanced MLD. Using the commercially available iso-butylphosphine (iBuPH$_2$ (a.k.a. **IBP**)) and cyclo-tetrasiloxane/silazane (**1**; **2**) as volatile precursors, deposition of thin films of phosphane-ene polymers was achieved. Thermal analysis of the precursors will be discussed, as well as the impact of varying pulse sequences, order of addition and surface priming agents (olefin appended acrylic acids). Pulse sequences of 300 or 600 cycles were employed (0.1 s pulse **IBP**, 10 s N_2 purge | 0.1 – 10 s pulse **1** or **2**, 10 s N_2 purge | 12 s Ar plasma @ 2800 W, 1 s N_2 purge), giving a GPC of 0.31-1.45 Å. All samples were characterized using XPS, ToF-SIMS and AFM. QCM experiments involving O_2 uptake will highlight the potential for these well-controlled polymer thin films for flexible electronic packaging. These results and future directions and opportunities will be discussed.

Key References:

[1] *Chem. Mater.* **2015**, *27*: 1412–1419; **[2]***Angew. Chem. Int. Ed*. **2018**, *57*: 13252-13256; **[3]** 'Photopolymerization of Primary phosphines with olefins to Generate Phosphorous Based Polymer Networks' File date (PCT): September 13, **2018** (PCT/CA2018/051136); Priority No: 62/558,093; **[4]***ACS Appl. Mater. Interfaces***2020**, *12,* 27640–27650; **[5]***Chem. Eur. J.***2020**, *26*, 12751-12757.

11:45am **EM-WeM2-5 Molecular Atomic Layer Deposition of Inorganic-Organic Hybrid Dry Resist for EUV Application**,
Su Min Hwang*, D. Le, Y. Jung, J. Veyan,* University of Texas at Dallas*; A. Subramanian, W. Lee,* Stony Brook University/Brookhaven National Laboratory*; N. Tiwale,* Brookhaven National Laboratory*; C. Nam,* Stony Brook University/Brookhaven National Laboratory*; M. Sung, J. Ahn,* Hanyang University, Korea (Republic of)*; J. Kim,* University of Texas at Dallas

Extreme ultraviolet lithography (EUVL) process is the most promising technique in advanced semiconductor manufacturing with scaling down of device feature size below sub-3nm.[1] However, there are several challenges to apply the EUVL in high volume manufacturing. One of these challenges is the resist performance. Compared to the current polymer-based resist, the development of new resist material is required to meet stringent requirements, such as high EUV absorption, resist thickness, and etch resistance. Among the various approaches, an incorporation of metal into organic resists has been recently reported.[1–3] In particular, hybrid 'dry' resists deposited using molecular atomic layer deposition (MALD) can be a promising approach.

In this study, we demonstrated the feasibility of inorganic-organic hybrid dry resist material comprising trimethylaluminum [$Al(CH_3)_3$] and hydroquinone ($C_6H_6O_2$) via the MALD process. In the temperature range of 150-200 ℃, the TMA/HQ hybrid film exhibited self-limiting growth behaviors (~0.48 nm/cycle) under various HQ exposure and TMA/HQ ratio. In the XPS depth profile with a gas cluster ion beam, the TMA/HQ films show consistent Al, C, and O composition, suggesting the uniform distribution of inorganic elements in the films. After understanding MALD characteristics, a detailed photochemical reaction of TMA/HQ hybrids during electron exposure was studied using a UHV chamber equipped with an *in-situ* FTIR, RGA, and electron flood gun system. The TMA/HQ hybrids with electron exposure above 200 eV exhibited the enhanced wet etch resistance using 0.1% AZ 300 MIF developer, suggesting that the TMA/HQ hybrids show negative-tone resists feature. In *in-situ* FTIR analysis with subsequent electron exposures, aromatic ring (C=C) and Ph–O bond peaks in HQ molecules decreased in intensity. It is expected that the aromatic ring in the HQ is activated via secondary electrons generated by Al, then crosslinked with adjacent HQ molecules. The detailed experimental results will be presented.

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[1] E.C. Mattson, et al., *Chem. Mater.* **30**, 6192 (2018).

[2] R. Fallica, et al., *J. Micro/Nanolithography, MEMS, MOEMS* **17**, 1 (2018).

[3] N. Tiwale, et al., *J. Mater. Chem. C* **7**, 8803 (2019).

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