Emerging Materials
Room Hall 3E - Session EM-WeM

Molecular Layer Deposition of Organic Materials and Organic-Inorganic Hybrid Materials

Moderators: Christophe Detavernier, Ghent University, Belgium, **Paul Poodt**, SparkNano

8:00am **EM-WeM-1 Resolving Composition and Crystal Structure of Fundamentally Novel MOF-Like Fe-Terephthalate Thin Films***, **Topias Jussila**, A. Philip,* Aalto University, Finland*; V. Rubio-Giménez,* Katholieke Universiteit Leuven, Belgium*; K. Eklund,* Aalto University, Finland*; S. Vasala,* ESRF - The European Synchrotron, France*; A. J. Karttunen,* Aalto University, Finland*; R. Ameloot,* Katholieke Universiteit Leuven, Belgium*; M. Karppinen,* Aalto University, Finland

Crystalline metal-organic framework (MOF) materials are anticipated for various applications due to their diverse material properties, yet they lack industry-feasible fabrication methods.[1] The atomic/molecular layer deposition (ALD/MLD) technique is in many aspects superior to the traditional solvent-based thin-film fabrication techniques of hybrid metal-organic materials, as it provides solvent-free thin films with precise thickness control and direct device integration. Most excitingly, the ALD/MLD enables the in-situ growth of even fundamentally novel MOF-like materials.[2] Iron-terephthalate (Fe-BDC) is one of the most appealing MOF materials and thus widely studied in bulk form owing to its attractive potential applications in photocatalysis, biomedicine, and beyond.[3]

Here we obtain through ALD/MLD in-situ crystalline, air-stable Fe-BDC thin films different from the Fe-BDC MOFs prepared in bulk form.[4] These thin films are characterized with a combination of advanced experimental and computational methods such as synchrotron grazing-incidence X-ray diffraction (GIXRD) and resonant inelastic X-ray scattering (RIXS) to disclose their unique chemical and structural features. The investigations reveal the existence of both Fe(III) and Fe(II) in the films and, excitingly, converge towards a novel crystalline Fe(III)-BDC phase with space group *C*2/*c* (Figure 1), and a previously unknown amorphous Fe(II)-BDC phase. Resolving the structure of a thin film material can be exceedingly demanding for materials with no bulk counterparts to compare with as traditional methods such as Rietveld refinement cannot be realized for thin films; this work provides a valuable example how the novel structures can be nevertheless determined.

References

1. C. Crivello, S. Sevim, O. Graniel, C. Franco, S. Pané, J. Puigmartí-Luis, and D. Muñoz-Rojas, Advanced technologies for the fabrication of MOF thin films. Materials Horizons 8, 168 (2021).

2. A. Tanskanen and M. Karppinen, Iron-terephthalate coordination network thin films through in-situ atomic/molecular layer deposition. Sci. Rep. 8, 8976 (2018).

3. D. Bara, E. G. Meekel, I. Pakamorė, C. Wilson, S. Ling, and R. S. Forgan, Exploring and expanding the Fe-terephthalate metal–organic framework phase space by coordination and oxidation modulation. Materials Horizons 8, 3377 (2021).

4. T. Jussila, A. Philip, V. Rubio-Giménez, K. Eklund, S. Vasala, P. Glatzel, J. Lindén, T. Motohashi, A. J. Karttunen, R. Ameloot, and M. Karppinen, Novel chemical bonding and crystal structure schemes in atomic/molecular layer deposited Fe-terephthalate thin films, Manuscript in preparation 2024

8:15am **EM-WeM-2 Molecular Layer Deposition of Metal Organophosphonate Thin Films***, **Aditya Chalishazar**, A. Dhara, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Molecular layer deposition (MLD) can be used to incorporate organic moieties in thin films, resulting in hybrid -----organic-–inorganic films [1,2]. Hybrid films are uniquely interesting due to the combination of the desirable properties of the organic and inorganic components [3]. However, MLD films often suffer from low chemical and hydrolytic stability, limiting their commercial success [4,5].

Phosphorus-containing hybrid materials (organophosphates) can be promising alternatives to conventional Si-based hybrid materials such as silicones. The stability of the P–O–M and P–C bonds [bond dissociation energy: P–C: 513 kJ/mol vs. Si–C: 435 kJ/mol] results in thermally and chemically stable hybrid materials. Among others, metal phosphonates are an interesting class of organophosphorus materials, with applications spanning ion exchange, proton conductors, anti-fouling coatings, catalysts and membranes. However, their deposition by MLD has yet to be explored.

We report the synthesis of novel hybrid aluminium phosphonate layers developed with MLD using trimethylaluminium (TMA) as the metal source and a novel phosphonate ester, dimethoxyphenylphosphonate (DMPP), as the phosphorus source. The growth of these films has been explored using two different dosing sequences (Figure 1) and studied with *in-situ* ellipsometry. At 250 °C, the three-step sequence yields a growth per cycle (GPC) of 0.4 Å/cycle, while the GPC of the four-step sequence was 0.8 Å/cycle. Both dosing schemes are observed to saturate (Figure 2a), with ALD-like growth above temperatures of 200 °C. The deposited films are characterised using FTIR (Figure 2b) and XPS, which establish the incorporation of the phenyl phosphonate components into the MLD film.

In view of applications, the temperature-dependent ionic conductivity of these films was explored from 100 to 400 °C, with the conductivity improving in a humidified environment (Figure 3a). The thermal (Figure 3b) and water (Figure 3c) stability of the films has also been studied, with the layers showing superior thermal stability (> 500 °C in air) and complete water stability after immersion for one hour. Finally, to verify the generality of this deposition approach, the organic group on the phosphonate backbone was varied, and the subsequent impact on the functional properties of the films was studied.

[1] ***Beilstein Journal of Nanotechnology***,**2014**, *5*, 1104
[2] ***Advanced Materials Interfaces***, **2022**, *9*, 2200210
[3] ***Chemistry of Materials***, **2001**, *13*, 3283
[4] ***RSC Advances***, **2015**, *5*, 29947
[5] ***Dalton Transactions***, **2016**, *45*, 1176

8:30am **EM-WeM-3 Europium-Organic Luminescent Thin Films for Bioimiging Applications***, **Amr Ghazy**,* Aalto University, Finland*; J. Ylönen, N. Subramaniyam,* Xfold imaging oy, Finland*; M. Karppinen,* Aalto University, Finland

The Förster resonance energy transfer (FRET) technique is currently employed in the biological detection of several viruses. In FRET, two chromophores are used, a donor and an acceptor [1]. Thanks to their intriguing luminescence properties, such as long lifetimes, and color pure sharp emissions, Ln^{3+} compounds are prime candidates as donor chromophores for FRET [2].

In FRET, the efficiency of energy transfer depends mainly on the distance between the donor and the acceptor chromophores. While the transfer becomes significantly weak when the distance is larger than 5 nm, no energy transfer occurs at 10 nm [3]. This leads to an issue when considering the typical Ln^{3+} materials in colloidal solutions. As being suspended in a mobile phase the distance between the Ln^{3+} donors and acceptors varies significantly. One solution is the use of a solid state immobile phase for the Ln^{3+} donors.

Atomic/molecular layer deposition has been recently utilized in developing Ln^{3+} photoluminescent thin films. However, these films usually require UV light as an excitation source, which can be detrimental to biological samples [4]. In our work, we developed a new process based on Eu^{3+} that can be excited by the less damaging visible light.

Thin films of Eu-HQA were grown from Eu(thd)3 as a metal precursor and 2-hydroxyquinoline-4-carboxylic acid (HQA) as an organic precursor. The process was developed at 210 °C, and yielded uniform films with a GPC of ~ 7.3 Å/cycle. The films showed a wide excitation wavelength range stretching between 185 nm in the UV region and up to 425nm in the visible light (fig. S1). These films can be deposited on various substrates, including glass and polymers, but most interestingly depositing on a plasmonic surface with complex structure (X-fold) is also possible. The plasmonic structure resonates with the excitation wavelength leading to a 20-fold increase in the emission strength of the films compared to the emission from similar film grown on plain Si substrates (fig. S2) .

Eu-HQA films on plasmonic surface can be used in combination with a FRET acceptor chromophore Alexa Flour 647 (AF) to show FRET emission. The films show the Eu^{3+} typical emission at 615 nm. Upon the addition of AF, the emission is transferred to AF, which emits light at 650 nm. This can be seen by a decrease in the intensity emission of Eu^{3+} at 615 nm, and an increase in the emission at 650 nm (fig S2).

References

[1] J. Rusanen et. al, Viruses, 2021,13 ,143.

[2] D. Geiβler and N. Hildebrandt, Curr. Inorg. Chem., 2011, 1, 17 —35.

[3] W. R. Algar et. al, Nat. Methods, 2019, 16, 815 —829.

[4] A. Ghazy et. al, Chem. Mater., 2023, 35, 5711 —6178.

8:45am **EM-WeM-4 ALD Young Investigator Award Finalist Talk: Inverted Living Molecular Layer Deposition: An Empowering Technique for Biomedical Applications***, **Karina Ashurbekova**, M. Knez,* CIC nanoGUNE BRTA, Spain

Polymeric molecules are born in an initiation process, they grow by a propagation process, and finally they 'die' in a termination process.

-SZWARC, M. ‘Living’ Polymers.*Nature* (1956).

This study shows an inverted living molecular layer deposition technique which facilitates controlled polymer growth with desired architecture, functional moieties, and adjustable properties.

We report on the first vapor phase growth of polyoxazolines (POx) through a living cationic ring-opening polymerization (CROP) mechanism. The two-step process includes a pulsed supply of a vaporized initiator (P-Toluenesulfonyl chloride) to a reactor space, which functionalizes a substrate by adsorbing as a molecular layer. This is followed by the chain propagation after the monomer is supplied and interacts with the layer of the chemisorbed initiator. We used three substituted oxazolines as monomers: 2-methyl-2-oxazoline, 2-phenyl-2-oxazoline and 2-isopropenyl-2-oxazoline. After exposing the substrate to the monomer vapors for several seconds the chamber is purged, and another portion of the vaporized monomer is introduced. With each monomer pulse, the thickness of the polymer layer increases until the monomer is consumed, which makes it possible to control the final thickness of the coating with the dose and the number of monomer feed cycles. The supply of water vapor to the reactor causes the growth to terminate. The living nature of the polymerization has been confirmed by *in situ* QCM studies. The composition, morphology, and thermal stability of the POxs have been evaluated by ATR-FTIR and XPS spectroscopies and thermogravimetric analysis (TGA).Although in this presentation we show only the growth of POx homopolymers, copolymerization via sequential monomer addition is also possible. The main advantages of this approach include absence of multicomponent solution-based impurities, thickness control, conformality and strong adhesion of the films to most substrates.

Extensive biological studies on biocompatibility, immunotoxicity, and control of protein and cell adhesion have provided positive results, underscoring the relevance of POx in biomedicine. (1) The demonstrated approach serves only as proof of principle and offers plenty of space for further investigation and adaptation of materials for specific applications. Thus, the present development is a starting point for a new way of surface functionalization with functional polymeric materials.

(1)Hoogenboom, R. (2009), Angewandte Chemie International Edition, 48: 7978-7994.

9:00am **EM-WeM-5 Hybrid Multilayer EUV Photoresist with Vertical Molecular Wire Structure***, **Myung Mo Sung**,* Hanyang University, Republic of Korea **INVITED**

Basic requirements for good patterns using extreme ultraviolet lithography (EUVL) are sensitivity, resolution, line edge roughness (LER), outgassing, etch resistance, defect density, and reproducibility. Among them, it has been proved that resolution, LER, and sensitivity (RLS) are interdependent with each other. The trade-off between RLS pose a critical challenge in the race towards device downscaling to 1 nm node. LER is the most important consideration to determine the manner in which EUVL will be employed. Recently, we develop a new EUV dry resist with organic-inorganic hybrid multilayer structures vertically tailored with several functional layers by using molecular layer deposition. Additionally, each layer includes a self-assembled organic monolayer to generate a vertical molecular wire structure. The hybrid multilayer resist shows high EUV sensitivity from the high EUV absorbing and reactive layers there. Furthermore, the vertical molecular wire structure of the hybrid resist generates exceptionally low LER.

9:30am **EM-WeM-7 Chemical Transformations Mediated by Low-Energy Electrons within Vapor Phase Synthesized Al-based Hybrid Thin Films for Advanced Resist Applications: An In-Situ Investigation***, **Dan Le**, T. Chu,* University of Texas at Dallas*; W. Lee,* Stony Brook University*; N. Tiwale,* Brookhaven National Laboratory*; J. Veyan, J. Kim, D. Kim, M. Lee,* University of Texas at Dallas*; C. Nam,* Stony Brook University/Brookhaven National Laboratory*; J. Kim,* University of Texas at Dallas

The adoption of higher (>0.55) or hyper (≥0.75) numerical aperture (NA) in EUV lithography is crucial for sustaining extreme downscaling of device features (<1-nm node), necessitating the adoption of novel resist platforms to meet the stringent demands.[1] Key targets of such EUV resists include achieving <20 nm thickness, homogeneity, mechanical and chemical stability, and high etch resistance.[1,2] However, attaining these essential targets using conventional spin-coating-based resists presents challenges. In this context, vapor-phase synthesized inorganic-organic hybrid dry resists offer advantages, in terms of ability to control resist thickness at the atomical scale and material homogeneity; and incorporating metal elements to enhance sensitivity, mechanical stability, as well as etch resistance.

Herein, we present a molecular atomic layer deposited inorganic-organic hybrid thin film system, consisting of TMA and HQ, for dry EUV resist applications, where negative tone resist characteristics were observed. Such characteristics of hybrid materials are reproducible at various electron energies (Fig. 1a-1c). Through *in-situ* FTIR and *in-operando* RGA analyses (Fig. 1d-1e), we elucidate the chemical transformations induced by electrons with energy as low as 80 eV, wherein the Al-based hybrid thin films underwent a dehydrogenation process and structural rearrangement, forming a crosslinked carbon network (Fig. 1f). Raman analysis further indicates that structural rearrangement of hybrid thin films leads to a formation of graphitic carbon domains (Fig. 1c).[3] Our study also reveals that the thickness degradation, upon exposure to the ambient condition, does not impede the patterning ability of the hybrid materials. The XPS and *in-operando* RGA spectra suggest that some of the additional C=O species formed during the aging period become volatile byproducts during electron exposures, thereby allowing the expected structural arrangement to proceed. Given the recent emergence of dry resists, the fundamental understanding of interactions between EUV photons/ primary and secondary electrons and resist materials is limited. Gaining insight into these chemical alterations as well as assessing hybrid material stability will undoubtedly contribute to the advancement of resist technology for future-generation lithography applications.

This work is supported by SRC, the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund, and NRF Korea.

[1] IRDS International Roadmap for Devices and System – 2023 Update Lithography & Patterning

[2] H. Suh *et al., Proc.* SPIE **12498**, 1249803 (2023).

[3] S. Lee *et al., Dalton. Trans.* **50**, 9958 (2021).

9:45am **EM-WeM-8 Molecular Layer Deposition of Phosphorus Thin Films Using Bis-α-aminophosphine Chemistry***, **Justin Lomax**, J. Bentley, P. Ragogna,* University of Western Ontario, Canada

Various organic substances like amides, ureas, terephthalates, and esters have been explored in molecular layer deposition (MLD), however the use of phosphorus-based precursors remains relatively unexplored.[1] One approach to synthesize P-containing polymer thin films, is to translate a solution phase process into a gas phase one. In this context, we have employed a primary phosphine, an imine and O_2/S_8 (Ch) to craft bis-α-aminophosphinechalcogenide materials.[2] Diazabutadiene (DAB) and primary phosphines (*i*BuPH$_2$ & CyPH$_2$) showed suitable precursor volatility for film deposition on primer functionalized SiOH surfaces. Depositions of films were carried out in a custom-built crossflow ALD reactor attached to a glovebox for air free handling (pulse/purge sequence: R-PH$_2$ 0.1 s/30 s; DAB 5 s/30 s; Ch 0.1 s/30 s). Additional surfaces of patterned Au/SiOH wafers were prepared to establish selectivity factors when using pre-functionalized surfaces. Small molecule synthesis, precursor volatility, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and Atomic Force Microscopy (AFM) techniques will be discussed.

(1) Meng, X. An Overview of Molecular Layer Deposition for Organic and Organic–Inorganic Hybrid Materials: Mechanisms, Growth Characteristics, and Promising Applications. *J. Mater. Chem. A***2017**, *5* (35), 18326–18378.

(2) Lamberink-Ilupeju, J.-W.; Willans, M. J.; Gilroy, J. B.; Noël, J. J.; Blacquiere, J. M.; Ragogna, P. J. Multicomponent Synthesis of Poly(α-Aminophosphine Chalcogenide)s and Subsequent Depolymerization. *Inorg. Chem.***2023**, *62* (37), 15104–15109.

Author Index

Bold page numbers indicate presenter