

Emerging Materials

Room Arveldeforum & Pedro de Gante - Session EM-MoP

Emerging Materials Poster Session

EM-MoP-2 Calcium and Vanadium Mixed Oxides With ALD, Fabian Krahl, K. Nielsch, Leibniz Institute for Solid State and Materials Research Dresden, Germany

Ternary oxides can show a wide range of very interesting physical properties and several have already been successfully deposited with ALD¹. One that, to our knowledge, hasn't yet been reported with ALD is CaVO₃, ALD-processes for calcium and vanadium oxides have been reported already in the early 1990s and 2000 respectively^{2,3}.

CaVO₃ is a correlated metal. These materials with strongly correlated charge carriers hold promise for a new type of transparent conductor (as opposed to highly doped wide bandgap materials like indium tin oxide)⁴. VO₂ and CaVO₃ also show a metal-insulator transition depending on film thickness which could make it an interesting phase change material⁵⁻⁷.

An ALD process of CaVO₃ could therefore be a great step towards the utilization and further research of this material because ALD is scalable and has great control over the thickness and composition of the deposited films. Here we want to present the status of our work with the ALD of CaO, V_xO_y and the mixed Ca_xV_yO_z Oxides.

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EM-MoP-3 Atomic Layer Deposition of Highly Pure Metals for Memory Devices Preparation, Haojie Zhang, B. Kalkofen, S. Parkin, Max Planck Institute of Microstructure Physics, Germany

Solid-state non-volatile memory devices have been seen as one of the most promising candidates to replace the state-of-the-art data storage media (e.g. hard disk drives). The expansion of memory devices from two-dimensional (2D) to three-dimensional (3D) can further increase the capacity and storage density of memory devices. Therefore, atomic layer deposition (ALD) of highly magnetic metals films is crucial for the design and preparation of 3D memory devices. In this work, we develop ALD recipes to deposit highly pure and smooth metals layers, including Pt, Co, and Ni. The deposited metal layers with optimized ALD recipes exhibit superior conductivity and magnetic property. Our developed recipes have huge potential to be used for other applications, such as batteries, renewable energy conversion.

EM-MoP-4 Liquid Atomic Layer Deposition of Cu₂(Bdc)₂(Dabco) Through 3D-Printed Microfluidic Chips, Octavio Graniel, D. Muñoz-Rojas, University Grenoble Alpes, CNRS, Grenoble INP, LMGP, France; *J. Puigmartí-Luis,* Departament de Ciència dels Materials i Química Física, Institut de Química Teòrica i Computacional, ICREA, Catalan Institution for Research and Advanced Studies, Spain

In recent years, liquid atomic layer deposition (LALD)¹ has emerged as a much simpler and versatile strategy to overcome some of the current constraints of its gas phase homolog for the deposition of metal-organic frameworks (MOF) thin films (e.g. thermal decomposition of precursors at high temperatures, poor control over the crystallinity).

This work describes the automated deposition of Cu₂(bdc)₂(dabco) thin films on silicon and glass substrates using a 3D-printed microfluidic chip. Films with preferred (001) and (100) orientations were obtained by changing the temperature of the reaction, the concentration of the reactants, and the dimensions of the microfluidic reactor as demonstrated by GIXRD measurements. In addition, the area of the thin film was successfully controlled by changing the flow rates of the precursors in a continuous flow mode.

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EM-MoP-7 Atomic Layer Deposition of Yttrium Iron Garnet (YIG) for 3D Spintronics, Michaela Lammel, Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science, Germany; *D. Scheffler,* Institut für Festkörper- und Materialphysik, Technische Universität Dresden, Germany; *D. Pohl,* Dresden Center for Nanoanalysis (DCN), cfaed, Technische Universität Dresden, Germany; *P. Swekis,* Max-Planck Institute for Chemical Physics of Solids, Germany; *S. Reitzig,* Institut für angewandte Physik, Technische Universität Dresden, Germany; *S. Piontek,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science, Germany; *H. Reichlova, R. Schlitz,* Institut für Festkörper- und Materialphysik, Technische Universität Dresden, Germany; *K. Geishendorf,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science, Germany; *L. Siegl,* Universität Konstanz, Germany; *B. Rellinghaus,* Dresden Center for Nanoanalysis (DCN), cfaed, Technische Universität Dresden, Germany; *L. Eng,* Institut für angewandte Physik, Technische Universität Dresden, Germany; *K. Nielsch,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science, Germany; *S. Goennenwein,* Universität Konstanz, Germany; *A. Thomas,* Institut für Festkörper- und Materialphysik, Technische Universität Dresden, Germany

During the last decade, three-dimensional (3D) nanostructures have gained increasing interest in the field of nanoscience. On the one hand, this development is driven by the desire to create ever denser microelectronic circuit structures. Truly 3D nanostructures will be key to go beyond stacked planar layers, which are commonplace in today's chip architectures. These structures then have electronic functionality in all three spatial directions, enabling for example ultra-high density memory concepts such as racetrack memory. On the other hand, nanoscale 3D structures bring along novel magnetization configurations and interesting physical effects arising from their "non-flat" geometry. Atomic layer deposition (ALD) is ideally suited for the fabrication of such truly 3D magnetic nanostructures due to its conformal coating capability.

We here demonstrate the fabrication of the ferrimagnetic insulator yttrium iron garnet (Y₃Fe₅O₁₂, YIG) via atomic layer deposition. YIG is a prototypical magnetic insulator used in the field of spintronics, since it combines a small coercive field, a large spin diffusion length and very low magnetization damping. We realize the ALD-based fabrication of YIG thin films by a supercycle approach based on the deposition of nanolaminates and show that our ALD-YIG films exhibit excellent structural and magnetic properties - comparable to those of high quality YIG thin films obtained by conventional, directional deposition methods. By validating the conformal 3D deposition of the ALD-YIG thin films, we highlight the usability of our ALD process for the fabrication of 3D nanostructures consisting of high quality YIG. Our findings provide the foundation for a variety of novel experiments on magnetic nanostructures using one of the best suited materials.

EM-MoP-13 ALD of Sulfide- and Selenide-Based Layered 2D Materials, Samik Mukherjee, K. Nielsch, Leibniz IFW Dresden, Germany

Layered two-dimensional (2D) materials exhibit many exotic physical, chemical, and electronic properties,¹ which allows them to create exciting new opportunities as a test-bed for many fundamental theories of materials science,^{2,3} as well as pave the path for a wide variety of applications, such as optoelectronic and nanoelectronic devices,⁴⁻⁶ clean energy harvesting,⁷ catalysis materials,⁸ bioengineering,⁹ and others. As an additional paradigm, a precise layering of quasi-2D building blocks of different materials in well-controlled sequences can provide an additional degree of complexity in terms of materials design and harnessing novel nano- and quantum-scale phenomena.

This work will discuss the current progress regarding the ALD synthesis of sulfides and selenides of tin, molybdenum, and tungsten on bare silicon and oxide-capped silicon (001) substrates. A comparative study, in terms of the structure, the morphology, and the growth rate of the films, for chloride and dimethylamido-based metallic precursors, will be presented.

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Some of the initial results of the ALD synthesis of 2D multi-layered films will be discussed. The work will also highlight the alteration to the crystal structure, morphology, and orientation of the as-grown films, brought about by post-growth annealing treatments.

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EM-MoP-14 Plasma Enhanced Atomic Layer Deposition of Scandium Nitride, Thomas Larrabee, G. Rayner, Kurt J. Lesker Company; N. Strnad, U.S. Army Research Laboratory; N. O'Toole, Kurt J. Lesker Company

Scandium nitride is a III-V semiconductor from group III and group XV, with properties distinct from those of more common III-Vs from group III and group XV.⁽¹⁾ Among the most important applications of ScN, however, is when it is alloyed with AlN to form Al_(1-x)Sc_xN. Thin films of Al_(1-x)Sc_xN have shown enhanced piezoelectricity⁽²⁾, and recently ferroelectricity⁽³⁾, enabling novel electronic devices, such as FE-FETs⁽⁴⁾. While ScN has been deposited by a variety of techniques including hybrid vapor-phase epitaxy (HVPE), magnetron sputtering, MBE, and MOCVD, an ALD technique would have advantages for CMOS integration --- including low temperature, wide-area uniformity, 3D conformality, precise thickness control, etc. While Sc₂O₃ ALD has been reported⁽⁵⁾, to the best of our knowledge, this represents the first example of ScN by an ALD technique.

Scandium nitride was deposited at 250 °C from tris(N,N'-diisopropylformamidinato)scandium(III) (Sc(amd)₃) and N₂/Ar plasma in a Kurt J. Lesker ALD150LX plasma-enhanced ALD reactor. The Sc(amd)₃ was delivered from a source held at 160 °C. XPS results demonstrate 1:1 Sc to N composition, with a small amount of carbon (3.8%) and very low oxygen in the bulk of the film (~1%). In nitride PEALD, ultra-high purity (UHP) process conditions have been shown to be necessary to obtain low oxygen content in readily oxidizable thin films, such as TiN⁽⁶⁾, which we believe is critical to low-impurity ScN PEALD. Grazing incidence X-ray diffraction (GIXRD) shows evidence of polycrystalline ScN at this growth temperature from a film grown on Si (with native oxide), with peaks corresponding to the (200), (220), (311), and (222) peaks of reference cubic ScN. A UHP process for ScN with compatible temperature window for PEALD of AlN, such as this, is anticipated to enable ultra-thin ALD-grown Al_(1-x)Sc_xN for applications in 3D piezoelectric MEMS devices and/or ferroelectric memory which would be difficult or impossible to achieve via existing non-ALD deposition techniques.

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EM-MoP-15 Yttrium Fluoride Coatings, Carlo Waldfried, Entegris, Inc.
There is a desire to produce ALD coatings of yttrium-fluoride materials, such as YOF and YF₃, but the implementation of such coatings is challenging and requires special considerations in the choice of precursor chemicals and reactants as well as ALD tool designs due to the corrosive nature of

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these processes. We will be presenting an approach to produce thin films of ALD-based YOF and YF₃ by depositing ALD Y₂O₃ and then converting the oxide film into YOF and/or YF₃ with a post-coat chemical vapor (non-plasma) conversion process. Utilizing this method YF₃ and YOF layers with thicknesses of more than 100nm have been produced and applied to high aspect ratio structures.

Film structure, composition, chemical bonding arrangement and morphology have been studied using techniques such as XPS, XRD, EDAX, and FIB SEM. It is believed that the fluoride is formed by an O → F exchange reaction, converting the Y₂O₃ into YF₃ or YOF.

Furthermore, we will discuss how blends of YF₃ and YOF, with a gradual transition of the composition from YF₃ to YOF and Y₂O₃ can be obtained and how that may be advantageous for the implementation of such fluoride coatings.

Hybrid Materials & Infiltration

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Hybrid Materials & Infiltration Poster Session

HM+EM+NS-MoP-1 Converting Electrospun Polymer Fibers Into Metal Oxide Nanofibers, Nanobelts, and Core-Shell Fibers via Sequential Infiltration Synthesis, R. Azoulay, M. Barzily, I. Weisbord, R. Avrahami, E. Zussman, Israel Institute of Technology, Israel; Tamar Segal-Peretz, Technion- Israel Institute of Technology, Israel

Sequential infiltration synthesis (SIS) has emerged in the past decade as a powerful technique for growth of inorganic materials within polymers through 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.

Here, we utilize SIS for high precision fabrication of AlO_x, ZnO, and AlO_x-ZnO core-shell fibers, with programmable dimensions, morphology, and surface structure. Designed growth profiles within the fiber are achieved through control over the precursors' diffusion depth within the polymer fibers. Long precursor diffusion times lead to moderate growth gradients and result in spherical fibers after polymer removal, while short precursor diffusion times lead to sharp growth gradients and result in fiber buckling into nanobelt morphology. To move towards complex inorganic fiber architectures, we extend single metal oxide SIS into spatially-controlled, multi-material SIS and demonstrate AlO_x-ZnO core-shell fibers with tunable core and shell thicknesses. The core-shell fibers are fabricated in a single SIS process, where the location of each metal oxide is controlled by its diffusion time. By harnessing the additional degrees of freedom of SIS, *i.e.* ALD-based growth within 3D polymer volume, we were able to achieve complex fiber morphologies.

HM+EM+NS-MoP-2 First Principles Modelling of Growth of Hybrid Organic-Inorganic Films, Arbresha Muriqi, M. Nolan, Tyndall National Institute, University College Cork, Ireland

Density functional theory (DFT) has proven to be a powerful tool to investigate the reaction mechanisms in hybrid film growth, predict the most suitable precursors and address aspects of the molecular layer deposition (MLD) experiments.

In our work, we use first principles density functional theory calculations to examine key steps in the mechanism of hybrid film deposition through MLD by modelling precursor-surface and precursor-precursor reactions and challenging the proposed reaction mechanisms in hybrid films. We explore the growth mechanism of aluminium, magnesium and titanium containing hybrid films known as alucones, magnesicones and titanicones, respectively. For alucones we investigate in detail the chemistry of the MLD process between the post-TMA (Al(CH₃)₃) pulse methyl-terminated Al₂O₃ surface with ethylene glycol (EG) and glycerol (GL). Double reactions of organic molecules with the alumina surface are also explored. We show that while both organic precursors react favorably with TMA fragments, EG and GL lie flat and create double reactions through the two terminal OH groups. For EG this phenomenon removes the active OH groups from the surface and growth will be less favorable while for GL the third OH group is available and growth can proceed.^[1] Because of the double reaction phenomenon of aliphatic molecules EG and GL, we proposed new aromatic molecules which due to their stiff backbone avoid the unwanted double reactions and lead to thicker and more flexible hybrid films.^[2] As the

infiltration phenomenon of TMA into the growing film is another common practical issue in alucone film growth, we consider DMAI ((CH₃)₂Al(OC₃H₇)) as an alternative to TMA. DFT calculations show that the reactivity of DMAI is sufficient for DMAI to take part in the MLD reactions. Combined with the fact that DMAI is a bulky molecule that avoids infiltration into the alucone film, DFT studies provide motivation to develop an MLD process using DMAI as inorganic precursor.

We also investigate the growth mechanism of titanicones grown using TiCl₄ and TDMATs metal source and EG or GL as organic reactants. We found that compared to TiCl₄, TDMAT adsorbs more favorably on the anatase-TiO₂, rutile-TiO₂ and Al₂O₃ surfaces and reacts more favorably with the organic species. Therefore, TDMAT is a more suitable precursor for titanicones film growth.

1. A. Muriqi, M. Nolan, First principles study of reactions in alucone growth: the role of the organic precursor, *Dalton Trans.*, 2020, 49, 8710 – 8721.

2. A. Muriqi, M. Karppinen M. Nolan, Role of terminal groups in aromatic molecules on the growth of Al₂O₃-based hybrid materials, *Dalton Trans.*, 2021, 50, 17583-17593.

HM+EM+NS-MoP-3 Hybrid Organic-Inorganic Isoporous Membranes with Tunable Pore Sizes and Functionalities for Molecular Separation, *Z. Zhang*, Helmholtz-Zentrum hereon GmbH, Germany; *Assaf Simon*, *T. Segal-Peretz*, Technion IIT, Israel; *V. Abetz*, Helmholtz-Zentrum hereon GmbH, Germany Block copolymers (BCPs) are considered promising materials for various membrane applications ranging from water treatment to protein separation due to their ability to self-assemble into highly ordered structures with uniform pore size and high pore density. Typically, the pore's size and surface interactions are controlled by the BCP chemistry. However, simultaneous control over both properties is difficult to achieve. In particular, reaching nanometric pores which will allow for molecular separation through the BCP chemistry is considered a major challenge.

In this study, we tailor the size and chemistry of BCP based ultrafiltration membranes by selectively growing metal oxides within and on the pores. Poly (styrene-*b*-4-vinyl pyridine) (PS-*b*-P4VP) was used to create ultrafiltration membranes in a process combining self-assembly with non-solvent induced phase separation (SNIPS). This results in one integral but asymmetric membrane, with ordered pores at the top of the membrane and sponge-like mechanically robust support layer at the bottom of the membrane. Sequential infiltration synthesis (SIS), an atomic layer deposition-based technique that enables selective growth of metal oxides inside the polar domains of BCP, was used to grow Al₂O₃ inside the P4VP domains of the BCP films. By incorporating metal oxides in the pores, the pore size can be reduced. By modifying the number of SIS cycles and/or the metal oxide we use, we can achieve control over the pore size while laying grounds for further membrane functionalization.

Functionality is achieved *via* straightforward scalable gas/liquid-solid interface reactions, where the hydrophilicity/hydrophobicity of the membrane is significantly changed by introduction of functional groups. The functionalized membranes reveal a superior selectivity and permeability to separate small organic molecules and fractionate similar-sized proteins based on size, charge and hydrophobicity.

This demonstrates the great potential of combining BCP and metal oxide growth for high-performance membranes for molecular separation. These membranes could be used in chemical and pharmaceutical processing as well as in other nanofiltration applications.

HM+EM+NS-MoP-4 Surface Functionalization of Porous Carbon Fibers by Vapor-Phase Methods for CO₂ Capture, *Stephan Prünfte*, Eindhoven University of Technology, Netherlands; *G. van Straaten*, *D. van Eyck*, *J. van Dijk*, *H. de Neve*, Carbyon, Netherlands; *M. Creatore*, Eindhoven University of Technology, Netherlands

The removal of excess CO₂ from the atmosphere will play a major role in the mitigation of global warming. While CO₂ sequestration at fossil fuel power plants is primarily achieved via wet chemical routes, CO₂ capture from ambient air is much more challenging. Solid-state adsorbents, consisting of CO₂-binding functional amine groups on porous supports, can deliver high CO₂ capture capacities with low energy requirements¹.

In this contribution, we report on the functionalization of porous carbon fibers by self-limiting vapor-phase techniques. Functionalization was carried out either via i) exposure to a cyclic azasilane molecule (2,2-dimethoxy-1,6-diaza-2-silacyclooctane) to introduce amine functionalities or ii) ALD of Al₂O₃ based on cycles of trimethylaluminum and H₂O followed by exposure to the azasilane molecule. Given the high specific surface area of the carbon fibers exceeding 1400 m²/g with a bimodal distribution of

pore diameter (0.5-0.6 nm and 0.8 nm), the above-mentioned precursors were dosed in multi-pulses.

The self-limiting nature of the two processes was verified by weight gain measurements. The increase in weight relative to the pristine sample saturated at 23% for direct amine functionalization. For case ii), the weight gain saturated at 11% for Al₂O₃ ALD and at 3.1% upon azasilane exposure relative to the pristine sample. The lower amine loading in case ii) with respect to case i), i.e. 0.14 mmol/g vs. 0.97 mmol/g, respectively, may result from clogging of smaller pores by ALD of Al₂O₃. XPS analysis confirmed amine functionalization, while EDX mapping of fiber cross-section revealed an homogenous distribution of Al and Si.

CO₂ capture capacities of 0.18 and 0.13 mmol/g_{sorbent} were measured under simulated ambient conditions by mass spectrometry for case i) and ii), respectively. The capture capacities were in the same range as those reported for amines grafted on SiO₂^{2,3}. However, the capture capacity with respect to amine loading for case ii) was 5-fold exceeding case i). This indicates that the functionalization of carbon fibers by ALD of Al₂O₃ and azasilane exposure leads to an efficient utilization of amine groups for CO₂ capture.

The presented research demonstrates the potential of modifying porous carbon fibers by grafting CO₂ adsorption functionalities via vapor-phase methods on the fibers' internal surface. Future engineering of porous materials by ALD and vapor-phase functionalization may pave the way towards realizing efficient direct air capture.

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HM+EM+NS-MoP-5 Mechanical Behavior of Hybrid Organic-Inorganic Thin Films Fabricated by Sequential Infiltration Synthesis (SIS), *Shachar Keren*, *T. Segal-Peretz*, *N. Cohen*, Technion, Israel

Hybrid organic-inorganic materials have drawn increased interest in the last decades due to their synergic properties. Control over the mechanical properties of hybrid organic-inorganic nanomaterials is central to their implementation in a wide range of applications, including energy absorbing materials and protective coatings. In recent years, sequential infiltration synthesis (SIS) has emerged as a promising new technique for fabricating hybrid materials with nanoscale precision. In SIS, inorganic materials are grown within polymers from vapor phase precursors using atomic layer deposition (ALD) chemistry. Several studies have demonstrated the potential of SIS to tune the mechanical properties of polymers. However, a full understanding of the relationship between the nanoscale structure and composition and the nanostructure mechanical behavior is still an ongoing effort.

In this research, we study the mechanical response of pristine and hybrid thin films fabricated via SIS using a combined experimental and theoretical approach. Hybrid thin films were fabricated by growing AlO_x within PMMA films via SIS process, using trimethylaluminum and H₂O as precursors. *In-situ* FTIR measurements were used to evaluate the interaction between the inorganic AlO_x and the polymer chains, and *in-situ* microgravimetric measurements were used to assess the inorganic mass gain. The mechanical responses were studied with nanoindentation combined with scanning electron microscopy (SEM). In addition, we developed a microscopic model which accounts for the hybrid organic-inorganic microstructure profile and correlates between the hybrid structures and their mechanical properties.

HM+EM+NS-MoP-6 Plasma Enhanced-MLD Processes of Phosphorus-Containing Thin Films, *Justin Lomax*, University of Western Ontario, Canada; *E. Goodwin*, *P. Gordon*, Carleton University, Canada; *C. McGuiness*, Solvay, Canada; *S. Barry*, Carleton University, Canada; *C. Crudden*, Queen's University, Canada; *P. Ragogna*, University of Western Ontario, Canada

Since the introduction of Molecular Layer Deposition (MLD), many compounds have been employed as a precursor to generate thin films of materials on the angstrom scale. Examples include amides, ureas, thioureas, azomethines, ethylene terephthalates, and ester precursors for thin film construction.¹ MLD films have been prepared with relatively few elements other than C, N, O, and S, leaving vast areas on the periodic table open for investigation. The Ragogna group has developed a method of preparing robust phosphorus polymer networks that in the bulk phase show excellent surface adhesion, barrier properties (O₂; H₂O), optical transparency (visible) and thermal stability (up to 400 °C).² This known method of generating polymer networks rich in phosphorus content was translated into an MLD process. By using plasma-enhanced MLD on Si/SiO₂

and Al₂O₃ substrates, film generation using the commercially available ¹ phosphine *i*BuPH₂ paired with a known volatile siloxane precursor (tetramethyltetravinylcyclotetrasiloxane) was explored. Thin film construction (10-100 nm) used an Ar radical source to facilitate P-H addition to the vinyl functionalities on the siloxane precursor and yielded a growth rate of 0.6 - 1.45 Å per cycle. Films were characterized by XPS, AFM and ToF-SIMS.

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HM+EM+NS-MoP-7 Al₂O₃ Dot and Antidot Arrays Fabricated by Sequential Infiltration Synthesis in Hexagonally Packed PS-*b*-PMMA Block Copolymer Thin Films, Gabriele Seguíni, A. Motta, M. Bigatti, F. Caligiore, CNR, Italy; G. Rademaker, A. Gharbi, R. Tiron, CEA/LETI-University Grenoble Alpes, France; G. Tallarida, E. Cianci, M. Perego, CNR, Italy

Sequential infiltration synthesis (SIS) is a three-dimensional (3D) growth process derived from atomic layer deposition (ALD) on polymers. SIS permits to grow inorganic materials into polymeric films. SIS into self-assembled block copolymers (BCP) offers the possibility to fabricate inorganic nanostructures starting from nanostructured organic templates. The fine-tuning of the dimensions of the resulting nanostructures can be achieved by proper selection of the SIS process conditions. In particular, the sequential reaction steps of the SIS process allow tuning the dimensions of the nanostructured material adjusting the number of SIS cycles. This capability to achieve a fine tuning of the dimensions of the resulting inorganic nanostructures is fundamental to make this technology suitable for the different target applications. At the same time, this step by step growth of the inorganic nanostructures allows to obtain information about the progressive mass uptake of the inorganic component into the polymer matrix and to delve into the growth mechanism.

In this work, Al₂O₃ dot and antidot arrays were synthesized by infiltration of trimethylaluminum and water precursors into out of plane cylinder forming poly(styrene-block-methyl methacrylate) (PS-*b*-PMMA) BCP thin films. The evolution of the characteristic dimensions of these inorganic nanostructures were investigated as a function of the SIS cycle number. Collected data provided information about the mechanism governing the effective incorporation of Al₂O₃ into the PMMA component of the BCP thin films. Accordingly, mass uptake of Al₂O₃ into the PMMA component of self-assembled PS-*b*-PMMA thin film is significantly enhanced compared to mass uptake in pure PMMA thin films, due to the presence of additional paths for diffusion of precursor molecules into the not reactive PS component and to their sorption at the PS/PMMA interface. Mass uptake is directly proportional to the surface of the PMMA nanodomains suggesting that in this specific BCP system the incorporation of Al₂O₃ into the PMMA component is essentially sorption limited. From the technological point of view, collected data demonstrate that SIS provides accurate control on the characteristic dimensions of the Al₂O₃ dot and antidot arrays.

This research was partially supported by the project "IONS4SET" funded from the European Union's Horizon 2020 research and innovation program (Grant No. 688072).

HM+EM+NS-MoP-8 Flexible and Conductive Zinc oxide – Zincone Nanolaminate Thin Films Deposited using Atomic and Molecular Layer Depositions, Seung Hak Song, B. Choi, Korea University, Korea (Republic of)

The combination of atomic layer deposition (ALD) and molecular layer deposition (MLD) enables the fabrication of various functional organic-inorganic composite thin film structures. By adjusting ALD and MLD cycles ratio, the structure of organic-inorganic thin films can be controlled. Therefore, the properties of the thin films can be tuned through the combination of various nano layers. Flexibility can be improved by inserting organic layers between thicker inorganic thin films. Incorporation of organic layers may degrade the electrical properties of thin films due to decrease in crystallinity. Therefore, it is necessary to study the thin film structures with optimal mechanical and electrical properties. Although the combination of ALD and MLD is very promising, few studies have been conducted. Especially, there are very few studies on the mechanical properties of organic-inorganic nanolaminate thin films, and studies have been conducted on very limited areas. We deposited zinc oxide (ZnO) –

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zincone nanolaminate thin films on transparent polyimide (TPI) using ALD and MLD methods and investigated their growth characteristics and mechanical-electrical properties with process conditions. We fabricated thin films with ZnO and zincone ratios of 100:1, 40:1 and 20:1 respectively, in the temperature range of 120 to 240 °C and measured the changes in mechanical-electrical properties according to deposition temperature and thin film structures. The mechanical properties of the thin films were measured through nanoindentation and bending tests. The bending test is a method to evaluate the durability of the thin films by measuring the change in electrical resistance of the thin films with bending radius, and it was possible to analyze the effect of zincone layers on the thin film's durability. In addition, changes in the microstructures of the thin films with process temperature were measured using X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the effect of microstructural changes on mechanical and electrical properties of the thin films were analyzed. From the tests results, as the zincone ratio increased, the crystallinity of the thin films decreased and the electrical conductivity was lowered, but the flexibility was slightly improved.

HM+EM+NS-MoP-9 Understanding of Polymer-Precursor Interactions during Sequential Infiltration Synthesis of Al₂O₃ in Polybutylene Succinate Films, Alessia Motta, G. Seguíni, C. Wiemer, IMM-CNR, Italy; R. Consonni, A. Boccia, SCITEC-CNR, Italy; G. Ambrosio, C. Baratto, INO-CNR, Italy; P. Cerruti, IPCB-CNR, Italy; S. Tagliabue, Corapack srl., Italy; M. Perego, IMM-CNR, Italy

The amount of plastic has increased exponentially over the years, leading to cumulative environmental damage in terms of microplastics pollution, soil infertility and impact on the wildlife. Therefore, the development of an alternative and sustainable option like bioplastics is highly recommended. In this respect, polybutylene succinate (PBS) is a commercial biodegradable and bio-based polymer with good mechanical properties, thermal and chemical stability. PBS presents good processability, and is used in different fields such as packaging, agriculture, and biomedical applications. However, PBS has poor gas barrier properties, and it is very stiff, limiting its use as a packaging material. The insertion of inorganic filler or the deposition of inorganic top layer have been proposed to modify its physical characteristics and to overcome these drawbacks. Sequential Infiltration Synthesis (SIS) is a sub-class of ALD and provides an attractive option for the preparation of inorganic-organic composites. SIS is based on the alternating exposure of the polymer to organo-metallic and oxygen precursors, diffusing and reacting into the organic material.

In this work, we investigated the growth of Al₂O₃ in freestanding ~30 nm thick PBS films by SIS process at 70°C via trimethylaluminum (TMA) and H₂O precursors. Through a systematic analysis of the composition and morphology of the infiltrated PBS samples at different process conditions, the reaction kinetics was clarified. FTIR and NMR measurements showed that the ester group is involved in polymer-precursors interaction, leading to the formation of a new aliphatic groups with the concomitant rupture of the main polymeric chain. Al₂O₃ incorporation in the infiltrated samples was further confirmed by the XPS analysis. Moreover, SEM-EDX cross sectional images showed a homogeneous Al₂O₃ distribution inside the PBS films, depicting a completely different scenario compared to standard ALD that determines Al₂O₃ growth on the more superficial region of the PBS film. Al₂O₃ mass uptake as a function of the number of SIS cycles was studied by infiltration in thin PBS films spin coated on Si substrates ranging from 30 to 70 nm. Mass uptake in the PBS films was found to be much higher than in standard polymethylmethacrylate films, at the same process conditions. Considering that the density of reactive sites in the two polymers is roughly the same, the observed difference in Al₂O₃ mass uptake is explained based on the different free volume of these polymers and the specific reaction mechanism proposed for PBS. These results pave the way towards the application of SIS for the improvement of bio-polymers for food packaging.

HM+EM+NS-MoP-10 On the Development and Atomic Structure of ZnO Nanoparticles Grown within Polymers using Sequential Infiltration Synthesis, Inbal Weisbord, M. Barzilay, Chemical Engineering Department, Technion, Israel; A. Kuzmin, A. Anspoks, Institute of Solid State Physics, University of Latvia; T. Segal-Peretz, Chemical Engineering Department, Technion, Israel

Sequential infiltration synthesis (SIS), an ALD-derived method for growth of inorganic materials inside polymeric structures, is an emerging technique for hybrid materials and inorganic nanostructure fabrication which can be utilized in a wide array of applications. In this work, we study the development of ZnO crystalline particles within SU-8, polymethacrolein

(PMCHO), and polymethyl methacrylate (PMMA) at the atomic scale. We probe the growth throughout diethyl zinc (DEZ)/H₂O SIS cycles, as well as after polymer removal. The crystalline ZnO structure is deciphered by combining two powerful methods: extended x-ray absorption fine structure (EXAFS) and high-resolution scanning transmission electron microscopy (HR-STEM). Synchrotron-based EXAFS provides large-scale statistical information on the crystals' long-range order and predicts their Wurtzite structure. HR-STEM of the hybrid polymer-ZnO films corroborates the predicted structure and allows for precise analysis of crystal size, orientation, and existing defects, as well as the dispersion of the particles inside each polymer. Significantly, the polymer matrix allows us to probe the growth, cycle-by-cycle, providing insights to ZnO atomic growth mechanism inside different polymers and extending our understanding of SIS. In addition, the methodology developed for such high-resolution imaging of hybrid films will allow future studies of additional hybrid systems.

HM+EM+NS-MoP-11 Fabrication of Hafnium Oxide Nanostructures Using Block Copolymer Matrices via Sequential Infiltration Synthesis, Przemyslaw Pula, University of Warsaw, Poland

Hafnium dioxide (hafnia, HfO₂) is a transition-metal oxide, an electrical insulator with a large energy bandgap ~5.5 eV. Among numerous applications of this material, its thin films have been used as gate insulators in transistors and as optical and corrosion-protective coatings. The scope of applications for porous hafnia nanostructures is even more extensive and includes catalytic and sensing applications.

Atomic Layer Deposition (ALD) is a powerful technique to fabricate thin oxide films with excellent uniformity and conformality on various substrates. While such layers may function as optical or protective coatings, a porous replica with a developed surface is more suitable for catalytic or sensing applications. The latter is readily available to fabricate via a variation of ALD, namely the Sequential Infiltration Synthesis (SIS). Although SIS shares chemical principles with ALD, the main difference is the volume growth of oxide within the polymer or photoresist molecules. Especially, block copolymers (BCPs) are a versatile platform for a synthesis of hybrid organic-inorganic nanostructures with tailored morphology and shape. More inorganic material can be infiltrated in a prolonged exposure step within a selected BCP functional group compared to a self-limited ALD surface growth. Despite the same chemical origin of these two techniques, not all ALD-derived compounds have been already demonstrated in SIS, mainly due to lower reaction temperatures required to sustain the order of a BCP template. Hafnium dioxide is an example of such a compound whose ALD process parameters were quite thoroughly examined while no SIS-derived experiment was successfully performed so far.

Here, we demonstrate the successful SIS block copolymer templated synthesis of a porous hafnium dioxide. The final effect was achieved by merging two factors: generation of more chemically reactive species combined with the increase of reaction temperature without a detrimental effect on the polymeric template order. We have verified the optimal synthesis parameters using an in-situ quartz crystal microbalance setup. The morphology and composition of our replica were investigated in SEM and XPS experiments, respectively.

Results indicated in this experiment show the successful synthesis of hafnia with the use of a large-molecule metal precursor which may catalyze further research in the topic and encourage to test similar compounds for other metals. The method presented here offers an option to modify soft matter samples in order to create hybrid organic-inorganic nanostructures, normally being damaged at standard operational ALD temperature conditions.

HM+EM+NS-MoP-12 ZIF-based Metal-Organic Frameworks for Cantilever Gas Sensors, Masoud Akbari, C. Crivello, O. Graniel, Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, France; M. Defort, S. Basraour, Univ. Grenoble Alpes, CNRS, Grenoble INP, TIMA, France; K. Musselman, Department of Mechanical and Mechatronics Engineering, University of Waterloo, Canada; D. Muñoz-Rojas, Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, France

Among the different gas sensing platforms, cantilever-based sensors have attracted considerable interest in recent years thanks to their ultra-sensitivity and high-speed response. The gas sensing mechanism in a dynamic cantilever sensor is based on its resonance frequency shift upon adsorption of a gas molecule on the sensor. In order to sensitize the surface of a cantilever, a sensitive receptor material with large surface area is required. Metal-organic frameworks (MOFs) are a class of nanoporous crystalline materials composed of metal ions coordinated to organic linkers. MOFs are promising for gas sensing applications as they have large

surface area, rich porosity with adjustable pore size and excellent selective adsorption capability for various gasses.[1] Zeolite imidazole frameworks (ZIFs) are a class of MOFs where metals with tetrahedral coordination (i.e. Zn, Co, Fe, Cu) are the central node and the ligands are imidazolate-based organic molecules.

In this work, we developed a ZIF-based thin film for dynamic cantilever gas-sensing applications. We employed a novel atmospheric pressure spatial atomic layer deposition (AP-SALD)[2][3] technique to deposit a ZnO sacrificial layer on the silicon cantilevers. This technique allows the deposition of high-quality films at atmospheric pressure, faster than conventional ALD. The ZnO layer was then converted to a particular ZIF film with desired porosity and size, through a MOF-CVD process.[4] A gas-sensing bench setup was developed for the cantilever actuation and read-out. We present the chemical and morphological properties of the ZIF, as well as the frequency response of the sensor to various gases. The device showed reliable sensitivity to humidity, CO₂ and several VOCs.

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HM+EM+NS-MoP-13 Tuning the Thermal Properties of Molecular Layer-Deposited Hybrid Metalcone Films via Modulating Metal Mass, M. Hoque, University of Virginia, USA; R. Nye, North Carolina State University; J. Tomko, University of Virginia, USA; G. Parsons, North Carolina State University; Patrick Hopkins, University of Virginia

Application of polymers as flexible substrates, interfacial binders, and encapsulation layers in electronic devices is often limited by their low thermal conductivities. In this work, we study the thermal properties of two hybrid organic-inorganic metalcone (alucone and tincone) films grown via molecular layer deposition. The thermal conductivity of the alucone and tincone films are measured via steady-state thermoreflectance and found to be 1.14 ± 0.18 and 0.4 ± 0.07 W m⁻¹ K⁻¹, respectively. The significantly higher atomic mass of tin compared to aluminum gives rise to this thermal conductivity difference. Furthermore, picosecond acoustics measurements reveal that the longitudinal sound speed, hence the bond strength is nearly the same between the two metalcone films. The thermal conductivity and longitudinal sound speed of the alucone and tincone films fill an important gap between the insulating soft polymers and thermally conductive, high strength polymers. Our study opens up new pathways for tuning the thermal conductivity of hybrid metalcone films without sacrificing the elastic properties.

HM+EM+NS-MoP-14 Analysis of Rearranged Organic/Inorganic Hybrid 2D Tincone Film via Molecular Layer Deposition, GeonHo Baek, S. Lee, H. Kim, S. Choi, J. Park, Hanyang University, Korea

In recent years, research on monolayer and two-dimensional (2D)-based family materials developed, starting with well-known graphene which has emerged an innovative research topic^[1]. Through atomic-level thickness control of ultra-thin 2D materials, the design and fusion of electronic devices are possible, enabling applications in various fields as well as in optoelectronics and semiconductors. Organic/inorganic hybrid tincone films were deposited by molecular layer deposition (MLD) using N,N'-tert-butyl-1,1-dimethylethylenediamine stannylene(II) as a precursor and hydroquinone (HQ) as organic reactants. When combined with HQ having a bi-functional hydroxyl group, SnO-based 2D hybrid tincone can be produced. In this study of tincone fabricated with a divalent precursor after a vacuum post-annealing process, the structural rearrangement of the SnO and the benzene ring bonds proceeded to form a SnO-based hybrid 2D structure. The rearrangement of the resulting structure occurred through

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π - π stacking (without pyrolysis) of the benzene ring. To understand the mechanism of fabrication of 2D hybrid tincone by π - π stacking of the benzene ring, and the strengthening of the crystallinity of SnO after the annealing process, the structural rearrangement was observed using X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffraction (GIXRD), grazing-incidence wide-angle X-ray scattering (GIWAXS), and Raman spectra.

As seen in the analyses, the as-deposited tincone originally had weak SnO nano-crystallinity without a specific crystal orientation. One hour after the annealing process at 400 °C, individual benzene ring bonds were combined with the SnO layer in a repeated arrangement of tincone monomer [-Sn-O-C₆H₄-O]_n. In the visible region (380–750 nm), high transparency (>85%) enabled optical device application through a hybrid layer with the SnO.

Reference

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HM+EM+NS-MoP-15 Molecular Layer Deposition (MLD) of Polyamide 6,4, Marina Borraz Casanova, CIC nanoGUNE, Spain

Nowadays innovation in food packaging is considered at the edge of studies to extend the shelf life of food packaging, and prevent microbial spoilage, chemical contaminants, moistures, etc. In order to confer such properties into these materials one of the very promising strategies is to use molecular layer deposition (MLD). In this work, the growth of thin films via MLD are obtained by using malonyl chloride (MC) and 1,6-hexanediamine (HD) as a precursor resulting in the in-situ synthesis of the compound designated as Nylon 6,4.

Herein we conducted detailed studies of different synthetic conditions (i.e., temperature, time, precursors, pulse, substrates). We observed by Fourier transform infrared spectroscopy (FTIR) the presence of characteristic peaks assigned to the final formation of Nylon. In addition, we prove a correlation of the growth of the thin film at increasing the number of cycles by studying the X-Ray reflectivity. These processed of coating suggest that the antimicrobial properties of the synthesized Nylon 6,4 can kill the bacteria's attached to the surface. Decreasing the amount of gram-positive (*Staphylococcus aureus*) and gram-negative bacteria (*Escherichia coli*) on the material surface.

In addition, the relevance of food packaging in the industry is moving towards smart packaging. This involves the ability to sense or measure an attribute of the product, the inner atmosphere of the package, or the shipping environment. Therefore, the ability to induce conductivity into these materials could be a key step for future generations.

This synthesis methodology can introduce new features to the materials, not only limited to food packing but also can be applied in other fields (i.e., textiles).

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 MOFs⁴⁻⁷ 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 group⁶, 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.

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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. Jousseume*, 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 Figure 1).

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. McGuinness*, 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 isobutylphosphine (iBuPH₂ (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 N₂ purge | 0.1 – 10 s pulse **1** or **2**, 10 s N₂ purge | 12 s Ar plasma @ 2800 W, 1 s N₂ purge), giving a GPC of 0.31-1.45 Å. All samples were characterized using XPS, ToF-SIMS and AFM. QCM experiments involving O₂ 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.

Wednesday Morning, June 29, 2022

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(CH₃)₃] and hydroquinone (C₆H₄O₂) via the MALD process. In the temperature range of 150-200 °C, 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.

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

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

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

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Emerging Materials

Room Auditorium - Session EM1-WeA

Emerging Materials

Moderators: Nathanaelle Schneider, CNRS-IPVF, Charles H. Winter, Wayne State University

1:30pm **EM1-WeA-1 Self-Limiting Growth of Monocrystalline GaN Films via Sequential Triethylgallium and Forming Gas Plasma Cycles in Hollow-Cathode Plasma-ALD Reactor**, *D. Shukla, S. Ilhom, A. Mohammad, B. Willis*, University of Connecticut; *A. Okyay*, Stanford University; *Necmi Biyikli*, University of Connecticut

Low-temperature synthesis efforts for high-quality GaN thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to stainless-steel based hollow-cathode plasma source revealed polycrystalline GaN films with preferred (002) orientation. Upon further modification of plasma source and reactor chamber design, eventually we achieved single-crystal GaN film growth on sapphire substrates. In this presentation we share our experimental findings on the epitaxial growth of GaN films using hollow-cathode plasma-assisted ALD (HCPA-ALD).

The films were deposited using triethylgallium (TEG) and forming gas (95/5% N₂/H₂) plasma as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed at 240 °C substrate temperature and 150 W rf-power. Both in-situ and ex-situ ellipsometry were employed to monitor the surface reactions, measure the thickness variation, and optical properties of the films. When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for GaN films on sapphire substrates showed a notable increase. Grazing-incidence XRD measurements revealed polycrystalline films on Si substrates while GaN/sapphire samples showed no crystal peak. When theta-2theta scans were done, we observed a strong single peak at (002) orientation, confirming the monocrystalline character of these GaN films. High-resolution transmission electron microscopy (HR-TEM) revealed the epitaxial relationship of the GaN layers grown on sapphire substrates. We attribute this significant improvement in crystal quality to the synergistic impact of customized HCPA-ALD reactor, large-diameter third-generation hollow-cathode plasma source, and optimized growth conditions with low-hydrogen forming gas plasma chemistry. With further improvement, we aim to achieve device quality electrical properties that can be used for prototype device fabrication.

1:45pm **EM1-WeA-2 ALD of In_{1-x}Ga_xN**, *Henrik Pedersen, P. Rouf, C. Hsu*, Linköping University, IFM, Sweden

Alloying group 13-nitrides to ternary phases allows tuning of the bandgap from 6.2 eV for pure AlN down to 0.7 eV for pure InN. The bandgap of In_{1-x}Ga_xN can theoretically span from UV to IR (3.4–0.7 eV), including the whole visible light range by varying x, making it promising material for optoelectronic applications. However, the ability to vary the composition of In_{1-x}Ga_xN is limited by the theoretically predicted metastability of In_{1-x}Ga_xN for 0.05 < x < 0.95, which leads to phase separation into their binary materials. The deposition of In_{1-x}Ga_xN is also hindered by the low thermal stability of InN, which decomposes into In metal and N₂ at around 500 °C, making traditional CVD approaches ill-suited. We have recently shown that ALD is a promising technique to deposit InN thin films with excellent structural quality,¹ ALD is therefore a promising alternative to CVD for In_{1-x}Ga_xN with x close to 0.5. In our efforts to deposit In_{0.5}Ga_{0.5}N we have explored two ALD approaches:

By using a short period superlattice, with alternating monolayers of GaN and InN, In_{0.5}Ga_{0.5}N deposition was attempted from repeated *n* InN and *m* GaN monolayers (*n*=*m*= 1, 2, 3...) using triethyl gallium (TEG), trimethyl indium (TMI) and ammonia plasma at 320 °C. This approach afforded single-crystalline In_{1-x}Ga_xN with tunable x between 0.3 and 0.7 by varying the ratio between *n* and *m*. The crystalline quality of In_{1-x}Ga_xN prepared by this multilayer approach ALD is remarkably better than that prepared by conventional continuous CVD and earlier reported ALD work using a multilayer approach with thicker layers of InN and GaN in the multilayer.

By mixing solid Ga(III) and In(III) triazenides in the same evaporator and co-subliming the two metal precursors In_{1-x}Ga_xN was deposited using a single, mixed metal pulse and NH₃ plasma at 350 °C.² In_{1-x}Ga_xN was successfully deposited using this approach and the value of x could be tuned by

changing the sublimation- and deposition temperatures, and the ratio of the two metal precursors. An In_{1-x}Ga_xN film with x = 0.5 was deposited and found to have a band gap of 1.94 eV. The In_{1-x}Ga_xN film grew epitaxially on 4H-SiC(0001) without need for a buffer layer and without phase segregation or decomposition of the In_{1-x}Ga_xN into the binary materials or In droplets.

Our results reveal a promising potential of ALD over conventional growth techniques to prepare ternary group 13-nitrides with tunable composition at low temperature, which provides the possibility to grow heterostructures with metastable alloys for device application.

Refs.

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2:00pm **EM1-WeA-3 Atomic Layer Doped Epitaxial β-Ga₂O₃ Films Grown via Supercycle and Co-dosing Approaches at 240 °C**, *Saidjafarzoda Ilhom, A. Mohammad, D. Shukla, B. Willis*, University of Connecticut; *A. Okyay*, Stanford University; *N. Biyikli*, University of Connecticut

Wide and ultrawide bandgap (WBG/UWBG) semiconductors make the backbone of high-power high-frequency electronics, used in electric vehicles, 5G and beyond wireless communication systems, and smart power grids. However, the relatively complex growth reactors and typical growth temperatures around 1000 °C lead to increased production costs. Gallium oxide (Ga₂O₃) is an emerging UWBG semiconductor showing superior material properties particularly ideal for harsh environment (high temperature, high-energy radiation, corrosion) applications. Reducing the growth and doping process temperatures for Ga₂O₃ would potentially enable a wider integration platform towards post-CMOS integration and flexible electronics.

Hence, we report on the low-temperature as-grown crystalline β-Ga₂O₃ films on Si, glass, and sapphire via hollow-cathode plasma-enhanced atomic layer deposition (HCPA-ALD). The films were deposited using triethylgallium (TEG) and Ar/O₂ plasma as metal precursor and oxygen co-reactant, respectively. Additionally, we have employed in situ atomic layer doping to n-type dope β-Ga₂O₃ films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. Growth experiments have been performed at 240 °C under 50 W rf-power. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Additionally, each unit ALD-cycle was followed by an in-situ Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both in-situ and ex-situ ellipsometry were employed to measure the thickness and optical properties of the films. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial β-Ga₂O₃ films with monoclinic β-phase. On the other hand, GIXRD of the samples grown on Si and glass displayed polycrystalline β-Ga₂O₃ films. Further outcomes from our ongoing optical and electrical characterizations will provide additional insight to overcome the challenges in achieving device quality undoped and doped β-Ga₂O₃ layers at low growth temperatures. A significant effort will be devoted for the comparison of Si and Sn-doping strategies, and if needed, ex-situ thermal annealing studies will be carried out for doping activation.

2:15pm **EM1-WeA-4 Closing in on Room-Temperature Metal-Insulator Transitions for Next Generation Electronics by Epitaxial Nickelate ALD**, *Linn Rykkje, H. Sønsteby, O. Nilsen*, University of Oslo, Norway

Complex oxides exhibiting metal-insulator transitions (MITs) are exemplar materials systems with strong correlation and emergent functional phenomena. Particularly the rare-earth nickelates (RENiO₃) with trivalent rare-earth RE = La, Pr, Nd, ..., Lu) are of interest as their MITs occur concomitantly with a structural transition. Underlying their rich phase diagram and the MIT's physical origin is a complex interplay of interactions; though it remains an unsolved puzzle in fundamental research, the exotic properties rooted in it have great potential for electronics applications.

Among the RENiO₃s, the MIT temperature of NdNiO₃ (T_{MI} = 200 K) is the closest to room temperature. Tuning the T_{MI} can be carried out using strain or by partial substitution of Nd with larger RE cations (see phase diagram). A more significant challenge, however, has been to develop a synthesis route that stabilizes Ni³⁺ and provides sufficient control under industrially relevant conditions. For instance, high temperatures and ultrahigh vacuum (UHV) typically facilitate epitaxy, but are incompatible with monolithic

device integration.

In this talk we show that with ALD – since long embraced by the electronics industry – we can grow high-quality epitaxial NdNiO₃ thin films with excellent control of thickness, uniformity, and chemical composition. This is achieved at low temperatures (225 °C) without constraints to the substrate geometry or need for UHV. Thin films of stoichiometric composition show low resistivities at room temperature and a sharp MIT, which are desired properties of a functional electronic switch in future neuromorphic architectures. Quaternary oxide thin films of the form (RE,Nd)NiO₃ have been successfully deposited using ALD with the aim of tuning the T_{MI} close to 273 K. Further chemical and electrical characterizations are needed, however, to establish and control the effect of partial RE substitution on the T_{MI}.

Although much of the fundamental behavior of the RENiO₃s remains contested, their potential for applications is undisputed; in fact, many members are already found in various device concepts. The success in using low-temperature ALD to grow high-quality NdNiO₃ (stoichiometric and cation substituted) thin films with a sharp MIT could promote the implementation of such switching-materials in next-generation electronics. A complex oxide field-effect transistor may thus be more within reach than previously anticipated, offering a viable alternative and/or complement to Si-based circuitry. Based on fundamentally different mechanisms, this could pave the path for a greener and more sustainable integrated circuit technology in the future.

2:30pm EM1-WeA-5 Plasma-Enhanced Atomic Layer Deposition of Spinel Ferrite CoFe₂O₄ and NiFe₂O₄ Thin Films, Mari Napari, University of Southampton, UK; M. Heikkilä, University of Helsinki, Finland; S. Kinnunen, J. Julin, University of Jyväskylä, Finland; T. Prodromakis, University of Southampton, UK

Thin films of insulating ferro- and ferrimagnetic complex oxides with high Curie temperatures, such as spinel ferrites, are essential for many emerging applications utilising room temperature spin-polarisation and magneto-optical effects, e. g. spintronics and sensors [1]. There is a need for a synthesis method for high quality magnetic oxides with large scale processing compatibility. Here, we have developed PEALD processes for two spinel ferrite materials, CoFe₂O₄ (CFO) and NiFe₂O₄ (NFO) using ferrocene and cobalt(III)- or nickel(II) acetylacetonate as precursors in direct plasma PEALD at 250°C. The CFO films were deposited with 1:2 Co:Fe ratio, while the NFO films were grown iron-rich to ensure that the ferrimagnetic property is not hampered by a parasitic antiferromagnetic nickel oxide component [2]. Stoichiometry of the grown ternary oxide films was confirmed with time-of-flight elastic recoil detection analysis measurements, which also showed that the low light element impurity content of the films (H < 2.0 at. %, C < 0.3 at. %) originates mainly from the acetylacetonate sources. According to the X-ray diffraction measurements of 40 nm thick films, the PEALD CFO and NFO have the desired (inverse) spinel structure, and the films grown on sapphire substrates are strongly (111) oriented already as-deposited. Helium ion microscopy and atomic force microscopy both showed that the films are continuous and free of aggregations. The oriented CFO films on sapphire have a very smooth surface (r_{rms} < 0.3 nm) but the NFO with a same thickness has a higher surface roughness (r_{rms} > 1.5 nm), which is in accordance with the previous observations of the ALD-grown iron-rich NFO [3]. In addition to the growth and structural characteristics we will present the results of the magnetic property measurements of the films.

[1] Hirohata et al. IEEE Trans. Magnetics 5 (2015) 0800511

[2] Napari et al. InfoMat 2 (2020) 769

[3] Bratvold et al. J. Vac. Sci. Technol. A 37 (2019) 021502

2:45pm EM1-WeA-6 Engineering Maxwell-Wagner Polarization in Al₂O₃/TiO₂/Al₂O₃ Nanolaminates Grown by Atomic Layer Deposition, Partha Sarathi Padhi, Raja Ramanna Centre for Advanced Technology, India; R. Ajimsha, S. Rai, P. Misra, Raja Ramanna Centre for Advanced Technology, India

Recently multilayered nanolaminates (NLs) of two dielectrics with conductivity contrast exhibiting giant dielectric constant owing to interface induced Maxwell-Wagner (M-W) relaxation have emerged as potential candidate for high density storage capacitors. The M-W polarization can be engineered precisely by controlling the thicknesses of sublayers and number of interfaces. We report growth of Al₂O₃/TiO₂ (ATA) NLs on Si and Au/Si substrates using atomic layer deposition, wherein M-W relaxation induced high dielectric constant was realized and engineered by tuning

sublayer thicknesses. Trimethylaluminum (Al (CH₃)₃) and Titanium tetrachloride (TiCl₄) were used as source for Al and Ti respectively, while deionized water (H₂O) was used as source for oxygen. Depositions were carried out at 200 °C and the average growth per cycle for TiO₂ and Al₂O₃ was ~ 0.4 and 1.6 Å respectively. The thickness of Al₂O₃ and TiO₂ layers were kept same in a given NL and was reduced from ~ 2.4 to 0.17 nm in different NLs keeping the total stack thickness fixed at ~ 60 nm. X-ray reflectivity curves from these NLs with intense Bragg peaks and clean Kiessig fringes, as shown in Fig. 1, confirmed the multilayer structures with uniform thickness along with distinct interfaces. The dielectric properties of ATA NLs were studied in Au/ATA/Au device configuration using impedance spectroscopy in frequency range of 10–10⁶ Hz. The dielectric constant of ATA NLs at 10 Hz was found to increase from ~ 23 to 290 with decreasing sublayer thicknesses from ~ 2.4 to 0.17 nm (Fig. 2(a)), while the dielectric loss was initially found to reduce from ~ 0.8 to 0.06 with reduction in sublayer thicknesses down to ~ 0.48 nm and then increased up to ~ 0.24 with further reduction in sublayer thicknesses down to ~ 0.17 nm (Fig. 2(b)). The dielectric constant of ~ 290 obtained for the ATA NL with ~ 0.17 nm sublayer thickness is significantly larger than that of both Al₂O₃ (K ~ 10) and TiO₂ (K ~ 20) and is proposed to be due to M-W type dielectric relaxation caused by space charge polarization across the interfaces of Al₂O₃/TiO₂. Temperature dependent dispersion in dielectric constant and loss of ~ 0.48 nm ATA NL clearly revealed two sets of thermally activated relaxations, confirming existence of interfacial M-W relaxation (Fig. 3). The ATA NLs of sublayer thickness ~ 0.17 nm showed high capacitance density of ~ 43.1 fF/μm², low loss of ~ 0.24 at 10 Hz, low EOT of ~ 0.8 nm, high breakdown field of ~ 0.265 MV/cm, low leakage current density of ~ 8.5 x 10⁻⁴ A/cm² at 1V and cut-off frequency of ~ 12KHz which are promising for development of next generation high density storage capacitors.

3:00pm EM1-WeA-7 Plasma Enhanced Spatial ALD of Silver and Copper Thin Films at Atmospheric Pressure using B₂O₃ Seed Layers, Tim Hasselmann, B. Misimi, University of Wuppertal, Germany; N. Boysen, Ruhr University Bochum, Germany; D. Rogalla, RUBION, Ruhr University Bochum, Germany; D. Theirich, University of Wuppertal, Germany; A. Devi, Ruhr University Bochum, Germany; T. Riedl, University of Wuppertal, Germany

Due to their excellent electrical and optical properties^{1,2} silver and copper thin films are used in various (opto-)electronic devices, e.g. as semi-transparent electrodes^{3,4}. Both of these metals have already been deposited using PE-ALD which provides a precise thickness control and homogeneous film growth at low temperatures⁵⁻⁹. However, since metals have a relatively high surface energy and thus tend to grow according to the Volmer-Weber-Mode¹⁰, most of the films consist of isolated islands instead of a percolated and conductive layer. Two possibilities to overcome these issue are the increase of the growth rate, since a correlation between growth rate and nucleation and thus percolation was observed, where a higher growth rate leads to earlier percolation^{6,8} and the use of seed layers to enhance the wetting of the deposited metal on the surface¹¹.

In this work, we provide detailed growth studies of Ag and Cu thin films grown from [Ag(NHC)(hmds)], [Ag(fod)(PEt₃)] and [Cu(NHC)(hmds)] precursors by spatial PE-ALD at atmospheric pressure. Interestingly, we find a significant effect of B₂O₃ seed layers on the growth of both metal films, compared to neat Si substrates. Specifically, for Cu films a substantially increased growth per cycle (GPC) of 2.1x10¹⁴ Cu atoms cm⁻² is found with a 10 nm thick B₂O₃ seed layer compared to a GPC of 3.3x10¹³ Cu atoms cm⁻² on neat Si substrates. At the same time the B₂O₃ seed layer strongly affects the percolation threshold and continuity of the grown metal layers. A comparison of Ag layers with a similar areal density of Ag atoms (~ 3x10¹⁷ Ag atoms cm⁻²) shows that on top of a B₂O₃ seed layer the Ag film is percolated with a high electrical conductivity, whereas its analogue on neat Si consists of separate islands and is found electrically insulating.

Detailed studies on the growth mechanism in dependence of the B₂O₃ seed layer will be presented and its potential use in area-selective ALD of metals will be discussed.

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3:15pm EM1-WeA-8 Silicon-Based Polymer-Derived Ceramic Coatings by Post-Processing of Pre-Ceramic MLD Thin Films, Kristina Ashurbekova, M. Knez, CIC nanoGUNE, Spain

Si-based polymer-derived ceramics (PDCs) belong to an emerging class of advanced materials that provide high strength, hardness, corrosion protection and heat dissipation, even upon use in extreme environments like high temperatures or chemically reactive plasma conditions. For example, wet-chemically synthesized aluminum doped SiOC PDCs retained their mechanical properties up to 1900°C in addition to an increased creep and corrosion resistance [1].

In the present work, MLD-deposited siloxane-alumina (SiAlCHO) thin films have been used as pre-ceramic polymers for a polymer-derived amorphous silicoaluminum oxycarbide (SiAlCO) synthesis by high-temperature post-processing. Pre-ceramic SiAlCHO films were grown by applying sequential surface reactions between 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V4D4) and trimethylaluminum [2]. To increase the mass yield during the polymer-to-ceramic transformation, cross-linking of the growing chains is desired. For this purpose, we introduced di-tert-butyl peroxide into the MLD process to cross-link the chains through their vinyl groups. The resulting film exhibited improved properties, such as 12% higher film density and enhanced thermal stability, if compared to the non-cross-linked film [3].

The fabrication of the final SiAlCO PDCs coatings was carried out by pyrolyzing the SiAlCHO MLD films in an Ar atmosphere and in vacuum at 900°C. The Raman spectra showed D and G peaks at 1350 cm⁻¹ and 1590 cm⁻¹, respectively, thereby indicating the formation of free sp²-hybridized carbon in the resulting PDCs film. The in situ sp²-carbon, formed by decomposition of Me and Vi groups in the SiO₂MeVi moieties within the SiAlCO PDC film was identified by X-ray photoelectron spectroscopy (XPS). The spectra showed presence of C=C sp² bonds and C-H bonds at the interface of free carbon nanoclusters. The elimination of a part of the organic groups is confirmed with the XPS survey scan data, where the Si:C ratio in the film after pyrolysis was reduced from 1:3 to 1.5:1. Transmission electron microscopy confirmed that the PDC film remained amorphous and defect-free after pyrolysis. Interestingly, annealing a 5 nm thick SiAlCO PDC film in vacuum at 900°C showed the formation of a conformal graphene shell on the surface of the amorphous SiAlCO PDC (Supplementary Fig. 1). This MLD-derived conformal SiAlCO PDC thin film showed exceptional uniformity, linear shrinkage, and thermal stability up to 1100°C.

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Emerging Materials

Room Van Eyck - Session EM2-WeA

Vapor Phase Infiltration

Moderators: Anjana Devi, Ruhr University Bochum, Maarit Karppinen, Aalto University

1:30pm EM2-WeA-1 Vapor Phase Infiltration of Polymers for the Synthesis of Organic-Inorganic Hybrid Materials: Process Kinetics, Chemical Pathways, and Final Hybrid Structure, Mark Losego, Georgia Institute of Technology

INVITED

Vapor phase infiltration (VPI) infuses polymers with inorganic atomic clusters to create unique organic-inorganic hybrid materials with novel chemical, electrical, optical, and mechanical properties. These new materials have been used in applications ranging from energy harvesting to filtration media to photolithographic hard masks. This talk will discuss our efforts to develop an appropriate phenomenological model to describe the VPI processing kinetics and our use of *in situ* gravimetry to validate this model. The talk will also explore our current understanding of the final hybrid structure and our use of electron microscopy, spectroscopy, and

density functional theory (DFT) to understand the inorganic's chemical state and its bonding structure to the polymer. Finally, several example applications will be discussed, and it will be shown how an understanding of the processing kinetics and chemical structure can be used to scale the VPI process to treat macroscale objects – including plastic components and textiles – as well as the additional complications and/or opportunities that

2:00pm EM2-WeA-3 Atomic Layer Deposition on Polymer Thin Films: On the Role of Precursor Infiltration and Reactivity, Robin Petit, J. Li, B. Van de Voorde, S. Van Vlierberghe, P. Smet, C. Detavernier, Ghent University, Belgium

Polymers play a role in a variety of applications owing to their flexibility, low toxicity and ease of processing. In many cases (e.g., lighting, photovoltaics, displays), they are incorporated into devices as host materials for electro-optical components (e.g., quantum dots), which are sensitive to the environment, i.e., moisture, oxygen and temperature. Polymers do not provide adequate protection, apparent from their high water vapor and oxygen transmission rates. To improve the stability, they are coated with barrier layers. We report on the use of Al₂O₃ ALD, with TMA and H₂O, to coat polymer thin films: polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate glycol) (PET-G) [1].

Polymers being complex molecular networks encompassing a free volume, this free volume causes a growth delay during Al₂O₃ ALD on polymers, calling for an understanding of the nucleation, precursor infiltration and polymer relaxation effects that impact this growth delay. Here, the reactivity of the polymers towards TMA is investigated with FTIR and XPS, while the extent of TMA infiltration as a function of deposition temperature is probed with in situ ellipsometry (SE).

Our results show that the temperature and presence, location and amount of polymer functional groups (C-O, C=O) influence the growth delay. While PS showed no infiltration, TMA-induced swelling was observed for PMMA and PET-G, with a change in reversibility as a function of temperature (Fig. 1). At low temperatures, TMA mainly physisorbs, while a pericyclic reaction drives the interaction with TMA for PMMA and PET-G at elevated temperatures (Fig. 2). For PET-G, this reaction can result in chain scission, accounting for the significant TMA infiltration. Furthermore, SE is used to determine the moment of closed layer formation, halting the infiltration and indicating the onset of linear growth (Fig. 3). The better understanding of the influence of the ALD deposition conditions and polymer properties on the barrier growth enables faster, more effective barrier creation for other ALD-polymer combinations.

[1] Petit, R. R.; Li, J.; Van de Voorde, B.; Van Vlierberghe, S.; Smet, P. F.; Detavernier, C. Atomic Layer Deposition on Polymer Thin Films: On the Role of Precursor Infiltration and Reactivity. ACS Appl. Mater. Interfaces 2021, 13, 38, 46151–46163.

2:15pm EM2-WeA-4 Obtaining Robust Hydrophilic Surface on Soft Polymer Through Atmospheric Pressure ALD, Albert Santos, B. van der Berg, V. van Steijn, R. van Ommen, Delft University of Technology, Netherlands

In the recent times, the use of modified soft polymer is increasing in a range of applications, such as biotechnology and medicine. Due to their flexible nature, good optical transparency, and high fidelity, soft polymers such as PDMS (polydimethylsiloxane) are known to be a good coating and microfluidics material. As a result, fields such as optical sensor, membrane separation, and bio-assays benefit tremendously. However, this polymer suffers from the lack of a hydrophilic group, limiting its application to several commercial potentials, especially in proper fluidic handling. Furthermore, research in obtaining robust hydrophilicity often involves changing the bulk material and/or extremely complicated processes. Therefore, there is a need for precise surface manipulation with relatively simple processes. Among many surface modification techniques, atomic layer deposition (ALD) is known for its atom-level control. Furthermore, its deposition on a polymer involves both surface reaction and infiltration, leading to formation of buffer layer without changing much of its bulk properties. This study focuses on the use of atmospheric pressure atomic layer deposition (APALD). Opposed to the conventional vacuum ALD, it makes the use of vacuum technology superfluous and at the same time allows convective transport to challenge the limitation in aspect ratio coverage. The results shows that deposition of 100 cycles form a 46nm layer of titanium oxide, of which the surface contact angle stays 74° over a period of 8 weeks. This is much more hydrophilic than bare PDMS (110°) and vacuum ALD (recovering back to 90°). Both scanning electron

microscopy and x-ray photoelectron spectroscopy depth profiling show that uniform deposition of surface and formation of mixed layer in the range of few microns are vital for preventing diffusion of uncured monomers to the surface, leading to more stable hydrophilic surface. Furthermore, this result is confirmed by washing some PDMS in organic solvent to reduce the amount of uncured monomer, resulting in a contact angle of 65° after 8 weeks. There are also little to no changes observed in the transparency and mechanical property. This study not only provides a novel and easy method to modify soft polymer such as PDMS, but also opens up various potential in the field of microfluidic coating and commercial layer deposition.

2:30pm EM2-WeA-5 Modified 3D Printed Architectures: Effects of Infiltration by Alumina on ABS, Atilla Varga, S. Barry, Carleton University, Canada

In recent years 3D printing has gained enormous popularity thanks to its affordability, accessibility, ease of use, and the ability to easily employ a variety of polymer materials. These potential polymer substrates are highly tunable in flexibility and strength which make them the ideal for printing filaments, they can incorporate metal powders, wood fibers, carbon fibers, and other composites.[1] The integration of 3D printing and industrial nanoscale processes such as ALD will have a significant impact in the development of advanced 3D printed architectures leading to a wide array of applications as currently being investigated.

Our group has previously shown improvement of solvent stability for 3D-printed acrylonitrile-butadiene-styrene (ABS) architectures using an alumina thin film.[2] We demonstrated a 30-50% increase in solvent exposure resistance with a ~200 nm thin film. In addition we observed infiltration in the ABS polymer when no thermal pretreatment was performed on the ABS architecture, with deposition carried out above the glass transition temperature.

Infiltration requires inherently different conditions than film deposition, specifically a longer exposure to the precursors, which ideally improves infiltration depth.[3] By infiltrating ABS rather than overcoating it with alumina, we will be improving the material's glass transition temperature (T_g). Various deposition parameters such as pulse length, soak time, and temperature have varying effects on the glass transition temperature and will be discussed.

The T_g of ABS could be improved by 10° C after the infiltration of alumina. Interestingly, this improvement was effective for only one heat-cool cycle. After cooling, the plastic reverted to its normal T_g. We speculate that this is caused by the plastic flowing together, out of the infiltrated alumina matrix. Scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX) will be used to examine the modified polymer structures (Figure 1). Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and conductivity probe measurements will be used to observe the physical property changes (focusing on T_g of the treated compared to the untreated polymer).

[1] T. Abudula et al., *Front. Bioeng. Biotechnol.*, **2020**, *8*, 586186

[2] Varga A. C., Barry, S. T., *J. Vac. Sci. Technol. A.* **2022**, accepted

[3] Robin R. P. et al., *ACS Appl. Mater. Interfaces* **2021**, *13*, *38*, 46151–46163

2:45pm EM2-WeA-6 Polymer-Inorganic Hybrids for Inducing Self-Healing Functionality in Metal Oxides, Oksana Yurkevich, E. Modin, CIC nanoGUNE, Spain; I. Šarić, M. Petravić, University of Rijeka, Croatia; M. Knez, CIC nanoGUNE, Spain

A rapid surge of research works is the commitment to the sustainability of mankind. However, the vast majority of these works are devoted to the self-healing of organic materials. At the same time, there is a growing demand for implementing this functionality to the inorganic materials due to the rapid development in the area of flexible electronics. The few existent examples for inorganic materials rely on liquid healing agents, such as liquid metals or liquid precursors. The progress in this field remains very challenging, mainly because of a lack of feasible healing agents and suitable ways to supply them to the damaged site. In this work, we propose an approach to form self-healing metal oxides (MeO) by applying the vapor phase infiltration (VPI) method.

We used VPI as a tool to induce self-healing properties into hybrid organic-inorganic materials. This was achieved by infiltration of metal organics into the polymers which do not possess reactive oxygen-containing functional groups. Application of a typical VPI process to a functional polymeric substrate will result in the formation of dispersed metal oxide clusters and nanoparticles (NPs) inside the polymer along with an inorganic thin film of the same MeO on the surface. This hybrid polymer matrix with dispersed

NPs can serve as a reservoir with healing agents for a repair of a cracked MeO film. Self-healing of inorganic materials and structures was realized also without liquid agents by making use of the mobility of inorganic NPs within polymers, as the spatial distribution of NPs can be tuned by means of harnessing both enthalpy and entropy.

After the infiltration process, samples were transferred into the microscope chamber and cut in a controllable way by a Focused Ion Beam (FIB). Usage of FIB and SEM allowed inspecting the ruptured area of the hybrid structure prior to and after its exposure to the ambient atmosphere. X-ray photoelectron spectroscopy (XPS), energy-dispersive x-ray spectroscopy (EDX), and transmission electron microscopy (TEM) were used to analyze the chemical structure and composition of the obtained hybrids. The self-healing effect after exposure of the FIB-cut sample to air was observed for zinc and indium metal oxides (Fig.1). Hereby, we introduce an alternative materials architecture and construction framework for designing inorganic materials capable to self-heal.

3:00pm EM2-WeA-7 Tailoring the Interfacial Interactions of Porous Polymer Membranes to Accelerate Atomic Layer Deposition: The Latent Path to Antifouling Membranes, Rahul Shevate, V. Rozyyev, R. Pathak, A. Mane, S. Darling, J. Elam, Argonne National Laboratory, USA

Atomic layer deposition (ALD) is a powerful strategy to engineer hybrid organic-inorganic membranes with emergent functionalities. The combination of atomic-level thickness control, wide materials palette, and unprecedented conformality allow the physicochemical properties (e.g., hydrophilicity) of mesoporous polymer membranes to be precisely tuned. The nucleation of ALD materials growth on polymer surfaces relies on chemical interactions between the ALD metalorganic precursor and functional groups in the polymer structure and these interactions dictate the number of ALD cycles required to achieve a continuous coating. Strategies to enhance these interactions could enable desirable properties such as anti-fouling behavior to be imparted on inert polymer surfaces that lack the necessary functional groups for ALD nucleation. In this study, we demonstrate that the reactivity of polyacrylonitrile (PAN) membranes towards ALD metal oxide (MO) precursors with Lewis acid characteristics is enhanced by introducing Lewis base functional groups (amidoxime: Am) on the PAN backbone. The resulting Lewis acid-base interactions accelerates the MO nucleation in Am-PAN and reduce the number of deposition cycles required to achieve hydrophilicity compared to the untreated PAN membrane. Unveiling the reaction mechanism, the in-situ FTIR intensity changes established enhanced interaction dynamics between the ALD MO precursors and the Am-PAN membrane, unlike the PAN membrane. For similar MO cycles, through both spectroscopic and thermogravimetric analysis, we observe enhanced MO loading in the Am-PAN membrane compared to the PAN membrane. Here we have verified that strong Lewis acid-base interactions led to enhanced loading for a range of ALD MO materials including Al₂O₃, TiO₂, SnO₂, and ZnO. Most importantly, the Al₂O₃-Am-PAN hybrid membrane showed 23.3% higher antifouling capability compared to the pristine PAN membrane. Our approach expands the scope of design options for fouling-resistant porous hybrid inorganic-organic membranes and may reduce manufacturing costs of water treatment membranes.

Keywords: ALD, membranes, metal-binding functionalities, water treatment, filtration, nanoporous structures

3:15pm EM2-WeA-8 Ruthenium Nanostructures via Sequential Infiltration Synthesis in Self-Assembled Diblock Copolymer Thin Films, Nithin Poonkottil, Ghent University, Belgium; E. Solano, ALBA Synchrotron, Spain; A. Muriqi, M. Nolan, Tyndall National Institute, University College Cork, Ireland; C. Detavernier, J. Dendooven, Ghent University, Belgium

Vapor phase infiltration or sequential infiltration synthesis (SIS) is an ALD-derived technique for creating organic-inorganic hybrid materials, by allowing ALD precursors and reactants to react within the free volume of soft materials like polymers. SIS on diblock copolymer (di-BCP) films is critical in lithography, where material growth is typically achieved selectively in one block while the other remains inert. A plasma treatment can be used to remove the organic components, resulting in nanopatterns that resemble the reacted block. However, metal nanopatterns derived from SIS are still in its infancy, as most reports focus on metal oxides, mainly Al₂O₃.¹

We present SIS of Ru² without any pre-treatment, using alternating infiltration of RuO₄ and H₂ in polystyrene-block-polymethylmethacrylate (PS-b-PMMA) templates, followed by plasma treatment to create patterns of Ru nanostructures (Fig.1A). Experiments on blank PS and PMMA films show that RuO₄ infiltration is selective (Fig.1B) into PS, with no significant

out-diffusion of RuO₄ from PS, and thus a strong interaction between RuO₄ and PS. Density functional theory calculations corroborate that PS-RuO₄ interaction is energetically favorable, whereas the PMMA-RuO₄ interaction is not. The inertness of PMMA is attributed to its compact structure with no sufficient space between units to accommodate RuO₄ molecules. *In situ* FTIR shows that aromatic CH and C=C bonds in PS are consumed during the RuO₄ infiltration. XPS depth profiles confirm the infiltration of Ru throughout the polymer. An enhanced morphology and density contrast between the PS and PMMA domains in the di-BCP films after infiltration is evident from scanning electron and atomic force microscopy (Fig.2), elucidating that a single SIS cycle can already considerably change the nature of the PS domains. In grazing incidence wide angle X-ray scattering images, the diffraction signals of Ru become more pronounced with increasing number of SIS cycles, confirming the crystalline nature of the infiltrated Ru nanostructures. A significant increase in crystallinity of Ru is observed after the polymer is removed by plasma, with clear diffraction peaks present even after a single SIS cycle. Finally, the formation of Ru nanolines resembling the di-BCP nanostructure after the plasma treatment is confirmed in AFM images (Fig.2).

1. Waldman et al., *J. Chem. Phys.* **2019**, *151*, 190901

2. Minjauw et al., *J. Mater. Chem C* **2015**, *3*, 132-137

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Emerging Materials

Room Van Eyck - Session EM3-WeA

Hybrid Coatings

Moderators: Christophe Detavernier, Ghent University, Belgium, Mark Losego, Georgia Institute of Technology

4:00pm **EM3-WeA-11 Photoactive Hybrid Materials by MLD, Ola Nilsen, P. Hansen**, University of Oslo, Norway **INVITED**

The sequential methodology of ALD/MLD allows for combinations of a remarkable wide range materials. This can be exploited in construction of photoactive materials, particularly for those based on multi-step processes like down and upconversion. Such materials relies on efficient processes for both absorbers, emitters and transfer of excited states while limiting non-radiative decay. It is clear that optimizing all properties simultaneously is not possible within a single material class.

With the ALD/MLD approach, we can combine highly absorbing organic molecules with fluorides and oxides and many more. By such manner, we have achieved complete energy transfer from the organic molecule terephthalic acid to Sm³⁺ without quenching. We also show drastic suppression of concentration quenching of multilayered structures of lanthanides as compared to solid solutions by confining energy migration in 2D planes. The flexibility of the MLD approach allows for exploration combinations of absorbers and emitters with a large variation in chemistry. Although one may be limited in the size of accessible molecules via the gas phase, the range may be quite large. This way of design allows combinations of otherwise incompatible species, both with respect to normally incompatible synthesis requirements and in controlling energy transfer and quenching routes.

4:30pm **EM3-WeA-13 Cerium (III) based Hybrid Inorganic-Organic Thin Films by ALD/MLD, Parmish Kaur**, Ruhr University Bochum, Germany; A. Muriqi, Tyndall National Institute, University College Cork, Ireland; J. Wree, Ruhr University Bochum, Germany; R. Ghiyasi, M. Safdar, Aalto University, Finland; M. Nolan, Tyndall National Institute, University College Cork, Ireland; M. Karppinen, Aalto University, Finland; A. Devi, Ruhr University Bochum, Germany

Ce-based hybrid materials are projected to be promising for applications such as catalysis, sensors, information storage, luminescent materials to name a few. However, they have been mainly developed by classical routes such as solvothermal and hydrothermal synthesis and thus suffer a major disadvantage of unwanted solvent molecules being trapped in the hybrid materials. Atomic/molecular layer deposition (ALD/MLD) is a solvent-free, gas-phase deposition technique for the deposition of hybrid organic-inorganic thin films which gives precise control over thickness, composition, and uniformity over large area substrates. Although one of the key factors of a well-functioning ALD/MLD process is the compatibility

of the employed organic and inorganic precursors in terms of volatility, thermal stability, and reactivity and this aspect hasn't been thoroughly investigated.

We have performed a systematic study to find compatible Ce and organic precursors for the growth of Ce-based hybrid thin films. This was realized by in-depth characterization of precursors, processes and supporting the findings by theoretical investigations using density functional theory (DFT). Thermal analysis studies showed that the precursors [Ce(dpdmg)₃], terephthalic acid (TPA), and hydroquinone (HQ) are sufficiently volatile and thermally stable to be deposited at 200 °C. Additionally, the reactivity of the precursors was modelled by DFT, which revealed the favourable reaction between inorganic and organic precursors. Thus, the combination of the chosen precursors was found to be compatible in terms of their matching physicochemical properties. The Ce-based hybrid thin films were deposited using [Ce(dpdmg)₃] as a source for Ce, while two different organic precursors, namely TPA and HQ, were tested as organic precursors yielding Ce-TPA and Ce-HQ hybrid thin films. The growth rate for Ce-TPA hybrid films was 5.4 Å cycle⁻¹ and for Ce-HQ hybrid films it was 4.8 Å cycle⁻¹ on Si(100) at a deposition temperature of 200 °C. FTIR studies confirmed the successful deprotonation of the organic precursors, the presence of metal-oxygen bonding, and the benzene ring vibrations in the hybrid films. Additionally, the Bader charge calculations predicted the oxidation state of the cerium in the films to be +3 which was further confirmed experimentally by XPS studies. Furthermore, XPS analysis confirmed the successful formation of Ce-O bonds. UV-Vis spectroscopy showed the π-π* transitions and LMCT transition present in the films, while the films are also UV absorbing. Hence, Ce-based hybrid thin films can be promising as redox-active or UV-absorbing materials.

4:45pm **EM3-WeA-14 Modifying the Physico-Chemical Properties of Polymer Nanofiltration Membranes with Metal Oxide ALD, Kirti Sankhala, T. Segal-Peretz**, Technion, Israel

Atomic layer deposition (ALD) is an emerging technology to tune the surface chemistry of membranes by providing conformal, smooth, and ultrathin coatings of various materials, such as metal oxides.^{1,2,3} The addition of an ultra-thin layer of metal oxides on a negatively charged polymer membrane surface offers enhanced surface energy and hydrophilicity with a possibility to fine-tune the pore size and reduce surface roughness.⁴

In this work, we enhance the chemical and physical properties of commercially available NF270 nanofiltration membranes by tin dioxide (SnO₂) coating via ALD. SnO₂ ALD was selected due to the high hydrophilicity and positive surface charge of SnO₂ among various metal oxides.⁵ In nanofiltration, the separations at the atomic or molecular scale are strongly influenced by electrostatic interactions and play a critical role in membrane performance. As ALD provides a conformal and nonporous coating layer, applying a large number of ALD cycles inevitably leads to pore blocking. However, a small number of ALD cycles (< 20) enables tuning of both the pore size and the pore chemistry.⁶ Several cycles of SnO₂ ALD, providing ca. 1-3 nm thick coating, increases the membrane's hydrophilicity, decreases its roughness, and reduces negative surface charges. This coating leads to higher salt rejection and salt selectivity with a slight decrease in membrane permeability. The morphological details of the hybrid inorganic-organic membranes obtained using scanning and transmission electron microscopies shed light on the conformal growth of SnO₂ ALD on the nanofiltration membranes.

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Wednesday Afternoon, June 29, 2022

5:00pm **EM3-WeA-15 Modelling of the Growth of Al₂O₃-Based Hybrid Films: Role of Terminal Groups in Aromatic Molecules**, *Arbresha Muriqi*, Tyndall National Institute, University College Cork, Ireland; *M. Karppinen*, Aalto University, Finland; *M. Nolan*, Tyndall National Institute, University College Cork, Ireland

Hybrid organic-inorganic materials fabricated using Molecular Layer Deposition (MLD) display unique properties and hold great promise for many technological applications. Much has been done in developing different MLD processes but much less is known about the growth mechanism in MLD films.

In this study we use first principles density functional theory (DFT) to investigate in detail the growth mechanism of hybrid films of aluminium oxide and aromatic molecules with different terminal groups deposited by MLD. We explore the reactions between the post-Al(CH₃)₃ (TMA) pulse methyl-terminated Al₂O₃ surface and homo- or hetero-bifunctional aromatic molecules with hydroxy (OH) and/or amino (NH₂) terminal groups: hydroquinone (HQ), p-phenylenediamine (PD) and 4-aminophenol (AP). DFT calculations show that the aromatic molecules bind favorably to TMA fragments via formation of Al-O, Al-N bonds and loss of CH₄. Importantly it is most favorable for the aromatic molecules to orient in an upright configuration, by avoiding the unwanted double reactions found for aliphatic diols, which will lead to thicker and more flexible hybrid films. We calculated a higher reactivity of the OH group with TMA compared to NH₂. However, aromatic molecules terminated with NH₂ groups are still an option to promote the film growth. We also explore the MLD chemistry with functionalised aromatic molecules to examine the influence of phenyl functionalization on the MLD chemistry. We found that we can modify the core of the aromatic molecules to target particular properties using specific chemical groups which promote the deposition of thicker and more stable hybrid films. Finally, we examine the reactions between the methyl terminated Al₂O₃ surface with new possible MLD aromatic precursors as hydroquinone bis(2-hydroxyethyl)ether and 1,1'-biphenyl-4,4'-diamine where DFT shows that the selected aromatic molecules react favorably with TMA fragments on the Al₂O₃ surface and are worthy of further experimental investigation.

[1] Arbresha Muriqi, Maarit Karppinen, Michael Nolan, Role of terminal groups in aromatic molecules on the growth of Al₂O₃-based hybrid materials, *Dalton Transactions*, 2021, 50, 17583-17593.

5:15pm **EM3-WeA-16 Engineering Biomimetic Biocompatible and Selectively Antibacterial Ultrathin Films by Vapor Phase Chemistry**, *Karina Ashurbekova*, K. Ashurbekova, CIC nanoGUNE, Spain; *A. Muriqi*, Tyndall National Institute, University College Cork, Ireland; *L. Barandiaran*, B. Alonso-Lerma, CIC nanoGUNE, Spain; *I. Šarić*, University of Rijeka, Croatia; *E. Modin*, R. Perez-Jimenez, CIC nanoGUNE, Spain; *M. Petravić*, University of Rijeka, Croatia; *M. Nolan*, Tyndall National Institute, University College Cork, Ireland; *M. Knez*, CIC nanoGUNE, Spain

This work describes a strategy for growing conformal ultrathin films of chitin and hybrid chitin-based biomaterials from the gas phase by Molecular Layer Deposition (MLD). We present a new class of organic-inorganic hybrid polymers, which we coin "metallo-saccharides", based on sugar monomers as precursors. For a controlled growth, we couple the monosaccharide N-Acetyl-D-mannosamine (ManNAc) with trimethylaluminum (TMA) or Titanium tetraisopropoxide (TTIP) from the vapor phase in repetitive cycles to obtain the respective biomimetic alumochitin or titanochitin thin films. The analysis of the resulting films was done by applying ATR-FTIR, X-ray photoelectron spectroscopy (XPS), Solid-state NMR (ssNMR), High resolution TEM (HRTEM) and Energy dispersive X-Ray spectroscopy (EDXS).

The evaluation of the antimicrobial activity of the alumochitin and titanochitin MLD films against Gram-positive (*Staphylococcus aureus*, *S. aureus*) and Gram-negative (*Escherichia coli*, *E. coli*) bacteria was assessed. The attachment of the bacteria and their proliferation on metallo-chitin-covered glass substrates, were analyzed by confocal microscopy. The results show a great antimicrobial activity of both alumochitin and titanochitin MLD films against gram-positive and gram-negative bacteria, making the films highly interesting for the fabrication of bioactive surfaces.

The biocompatibility of both alumochitin and titanochitin hybrid MLD films was characterized by testing the *in vitro* proliferative behaviors of HEK (Human Embryonic Kidney) 93 human cells cultured on the substrates. We mainly focused on the cell attachment and proliferation. All MLD-coated substrates showed higher cell proliferation than the reference samples, namely uncoated coverslips.

The chemical interactions between the precursors ManNAc and TMA or TTIP, and the probability of the hybrid alumochitin or titanochitin film formation were modeled by density functional theory (DFT) and showed energetically favorable reaction mechanisms.

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