Tuesday Afternoon, August 6, 2024

Emerging Materials
Room Hall 3E - Session EM-TuA

Vapor Phase Infiltration

Moderators: Jolien Dendooven, Ghent University, Belgium, **Sang In Lee**, Synos Foundation

4:00pm EM-TuA-11 Selective Deposition of Al₂O₃ on Patterned Polymer Substrates using Vapor Phase Infiltration, *Maggy Harake, Y. Lee,* Stanford University*; B. Yu,* Lawrence Berkeley National Laboratory*; G. D'Acunto,* Stanford University*; R. Ruiz,* Lawrence Berkeley National Laboratory*; S. Bent,* Stanford University

As semiconductor lithography nears sub-10 nm feature sizes with the upcoming adoption of high numerical aperture extreme ultra-violet lithography, patterning materials that enable these small dimensions are not the only challenge. Lithographic materials must facilitate high-precision pattern transfer and ensure uniform feature sizes with minimal placement errors thereby mitigating the stochastic variations that limit density scaling. We have recently introduced a concept of area-selective deposition (ASD) with vapor phase infiltration (VPI) akin to atomic layer deposition, which is a promising tool for high-precision patterning.

Our approach involves utilizing a patterned *two-color* surface modification monolayer, where regions of the *first color* serve as non-growth surfaces resembling conventional ASD schemes, while regions of the *second color* act as growth promoters through enhanced VPI. We engineer the *two-color* surface modification layers by leveraging the versatility and lithographic compatibility of graft-to-polymer brushes.

This work reports on the selective infiltration of Al₂O₃ using VPI on patterned substrates coated with growth-promoting sequence-defined polypeptoid (PP) polymers and polystyrene brushes (PS) (non-growth surface). We investigate PP side-chain chemistry to determine which monomer combinations are most receptive to ALD precursors and gain insight into how to tune the thickness of the oxide film. Furthermore, we consider how three Al precursors (triethylaluminium, trimethylaluminum (TMA), and dimethyl aluminum isopropoxide (DMAI)), which vary in ligand type and size, interact with and influence growth within the polymers and lead to different oxide film densities.

We confirm successful growth of the oxide film on the PP surface of the substrate using atomic force microscopy (AFM). Additionally, blanket substrates covered with PP or PS polymer brushes show large variations in Al uptake and selectivity, as determined by x-ray photoelectron spectroscopy (XPS) and angle-resolved XPS, depending on the ALD precursor-PP interaction. From XPS we determine that TMA creates a thick oxide film within PP and not in PS. DMAI, the larger molecule of the three and the only one containing an Al-O bond, is shown to not be selective between the two types of polymer brushes. In-vacuo infrared spectroscopy measurements provide mechanistic insight into the reactions with the various precursors. Finally, upon reactive ion etching, we demonstrate successful pattern transfer from the VPI-hardened polymer pattern onto the substrate, providing a bridge for existing patterning technologies to be paired with this selective process.

4:15pm EM-TuA-12 Sequential Infiltration Synthesis of Al₂O₃ in PMMA and PLA Thin Films: Convergence of Results Across Experimental Data and Theoretical Studies, *Michele Perego,* CNR-IMM, Agrate unit, Italy*; A. Motta, G. Seguini, C. Wiemer,* CNR-IMM, Agrate Unit, Italy*; K. Ronnby, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Sequential infiltration synthesis (SIS) is a vapor phase infiltration technique for the creation of organic-inorganic hybrid materials and/or inorganic nanostructures from a suitable polymer template. So far, the number of inorganic materials that can be grown by SIS is quite limited. To expand the materials library and widen the application fields, studies on kinetics, diffusivity, reaction energy and mechanism are necessary.

In this work, Al₂O₃ is infiltrated in poly (methyl methacrylate) (PMMA) and poly (lactic acid) (PLA) thin films by means of a standard ALD reactor, operating at 70°C in quasi-static mode, using trimethyl aluminium (TMA) and water. Selected polymers are characterized by the presence of ester groups that are expected to act as reactive sites for TMA. In situ spectroscopic ellipsometry reveals that significant swelling and deswelling of PMMA occur during TMA exposure and purging, respectively, due to sorption and subsequent desorption of TMA molecules that are not stably incorporated into the PMMA matrix. PLA exhibits a much larger swelling than PMMA during TMA exposure, but no significant deswelling is observed during purging, suggesting that a large amount of infiltrated TMA molecules is effectively trapped into the polymer matrix by a stable chemical bond. Accordingly, ex-situ XPS analysis demonstrates that much more Al₂O₃ is grown in PLA than in PMMA. Additionally, ex-situ XPS analysis indicates that, in both cases, TMA incorporation occurs through the formation of an Al-O covalent bond at the C-O-C group, as already observed in other biopolymers.

Two density functional theory (DFT) approaches were used to investigate the infiltration of TMA into PMMA and PLA polymers. Binding configurations and energies were modelled using a gas phase model of a ten-unit polymer. For both polymers, TMA was found to form an adduct with the oxygen in the C=O with an exothermic reaction energy, consistent with experiment. Furthermore, TMA was able to exothermically insert into the C-O-C bond of PLA, forming a covalent Al-O bond, aligning with the ex-situ XPS results. Infiltration modelling employed a periodic model with two eight-unit polymer chains. Both PMMA and PLA displayed swelling upon TMA infiltration, saturating with increasing TMA, consistent with experimental findings.

This combined experimental and theoretical study provides insight into SIS of Al₂O₃ in PMMA and PLA. The methodology can be extended to other precursors or polymers, unravelling of the complexities of SIS at the molecular level.

4:30pm EM-TuA-13 Expanding the Toolbox of Vapor Phase Infiltration Processes, *Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel **INVITED**

Vapor phase infiltration (VPI), also named sequential infiltration synthesis (SIS), is a technique derived from ALD that enables the incorporation of inorganic species into polymeric matrices. VPI can modify the properties of polymers by creating hybrid organic-inorganic materials with enhanced mechanical, electrical, optical, or catalytic functionalities. In addition, polymer patterns can be used as templates for confined growth, enabling simple conversation of organic nanostructures into inorganic ones, upon polymer removal. With these abilities, VPI is an appealing technique for a wide range of applications- from nanopatterning and sensing to energy storage devices and water filtration membranes. To continue expanding VPI processes, key challenges need to be addressed. These include new VPI chemistries, better understanding and control over growth processes and depth gradients, as well as new polymer chemistries, morphologies, and architecture for VPI.

Here I will describe our efforts in addressing these challenges. To expand VPI chemistries, we demonstrated the use of TDMA ligands in VPI, creating SnO₂ and HfO₂ nanostructures from block copolymer templates. Despite the large volume of these precursors that reduce diffusion through the polymer, exploring the parameter space of VPI enabled us to rationally design these processes. We also explored new ways for fabricating multi-material structures via VPI by controlling either the precursors' diffusion or their ratios in a three-precursor process, leading to spatially controlled structures and doped metal oxides. We investigated ZnO nucleation and growth in an array of polymers, setting design rules for this important VPI process. Finally, we demonstrate how this knowledge can be harnessed for a new application- protecting degradable polymers from UV radiation. We show how VPI can enhance the growth of ALD on the polymer surface leading to the synergic effect of high durability of these sensitive polymers under destructive UV radiation.

5:00pm EM-TuA-15 Organic-Inorganic Hybrid Thermoelectric Materials Through Vapor Phase Infiltration, *Kristina Ashurbekova,* CIC nanoGUNE, Spain*; M. Naumochkin, H. Reith, K. Nielsch,* Leibniz Institute for Solid State and Materials Research (IFW), Germany*; M. Knez,* CIC nanoGUNE, Spain

The fabrication of a multiplicity of hybrid thermoelectric (TE) materials is limited by the fabrication methodologies and incompatibilities of the involved materials classes. We present a new set of hybrid materials with covalently bound organic/inorganic interfaces by growing Sb₂Te₃, Sb₂Se₃, Bi₂Te₃, Bi₂Se₃ inside the bulk of the semi-conducting polymer Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) by vapor phase infiltration (VPI). In this work, we focus on the p-type Sb₂Te₃-PEDOT:PSS. SbCl₃ and (Me₃Si)₂Te were used for the VPI growth of Sb₂Te₃ inside the bulk of the spin-coated polymer. SEM, SIMS and XPS results showed Sb₂Te₃ infiltration throughout the whole 200 nm polymer depth. TEM showed the rhombohedral phase of Sb₂Te₃ grown in the bulk and on top of the polymer. TE characterization of the hybrids over a temperature range of 293–433 K was performed with a lab-on-chip ZT test platform

which allowed simultaneous characterization of all in-plane parameters of the films, including the electrical conductivity (σ), Seebeck coefficient (S), thermal conductivity (λ_{total}), Hall coefficient R_H, and the thus derived Power Factor (PF) and ZT. TE characterization was performed over several heating-cooling cycles (293–433 K), until equilibrium of the measured parameters was reached. Interestingly, during the first three heating-cooling cycles, the difference in σ between each measurement increased to values of more than 80 S cm^{-1}, changing from semiconducting behavior to metallic. This likely originates from migration and crystallization of the inorganic phase in the polymer that leads to formation of additional conductive paths. The thermal transport behavior supports this idea, showing a delta λ_{total} decrease by 0.3 W m^{-1} K^{-1} with thermal cycling. This indicates that the degree of disorder increases through formation of out-of-plane Sb_2Te_3 crystals. Decoupling of σ from λ_{total} is related to suppression of the lattice λ by enhancing the boundary-scattering events for heat-carrying phonons. At the same time the chemical bonds in Sb_2Te_3-PEDOT:PSS are promoting the direct electronic interaction between the inorganic and organic phases, facilitating electron transport. Finally, a great increase in S to a value of 135 μV K^{-1} at 293 K was achieved, much higher than the intrinsic S of PEDOT:PSS (20 μV K^{-1}). A remarkable PF of 610 μW m^{-1} K^{-2} was obtained at 433 K, corresponding to σ of 250 S cm^{-1}. The results offer new solutions for energy harvesting technologies with high flexibility. *K.A. acknowledges MSCA IF fundings, No:101032113.*

5:15pm **EM-TuA-16 Surprising, Simultaneously Enhanced H$_2$/CO$_2$ Selectivity and H$_2$ Permeability in Polymer Gas Separation Membranes by 1-Cycle Alumina Atomic Layer Deposition: The Effects of Inadvertent Vapor-Phase Infiltration**, *L. Hu,* University at Buffalo*; W. Lee, A. Subramanian,* Stony Brook University*; E. Deng,* University at Buffalo*; K. Kisslinger,* Brookhaven National Laboratory*; S. Fan,* University of Colorado Boulder*; V. Bui,* University at Buffalo*; Y. Ding,* University of Colorado Boulder*; H. Lin,* University at Buffalo*; **Chang-Yong Nam**,* Brookhaven National Laboratory

For polymer gas separation membranes that typically rely on the molecular sieving effect, an improved selectivity typically accompanies a lowered permeability, thus limiting a simultaneous improvement of the two parameters (i.e., Robeson upper bound). Here, we discover that polybenzimidazole (PBI), one of the leading membrane materials for H$_2$/CO$_2$ separation, can exhibit simultaneously increased H$_2$ permeability and H$_2$/CO$_2$ selectivity, surpassing the Robeson upper bound, once treated by simple, low-temperature (85 °C) 1-cycle alumina atomic layer deposition (ALD).[1] We find that the normal 1-cycle alumina ALD (i.e., not using an intentional exposure-mode protocol), comprising 15 msec sequential dosing of trimethylaluminum (TMA) and water with 10 sec intermediate purging, leads to a surprising vapor-phase infiltration (VPI) of alumina into PBI matrix, penetrating over several micrometers deep into the film. The resulting AlO$_x$-doped PBI hybrid membrane features remarkably increased H$_2$ permeability by 120% - 270% and H$_2$/CO$_2$ selectivity by 30% at 35 - 200 °C, compared to the untreated control. This unusual, simultaneously enhanced H$_2$ permeability and H$_2$/CO$_2$ selectivity were attributed to the disrupted PBI polymer chain packing by the AlO$_x$ infiltration, which was found to be mediated by the reaction between infiltrating TMA and amine groups available in PBI. The suggested mechanism was further supported by the TMA-only-infiltrated PBI membrane that displayed a similarly increased H$_2$ permeability. Given the simple and fast treatment protocol, this demonstration showcases a facile and scalable way of utilizing ALD and VPI for engineering and improving polymeric membranes important for CO$_2$ capture and future H$_2$ economy.

[1] L. Hu et al., "Few-cycle atomic layer deposition to nanoengineer polybenzimidazole for H$_2$/CO$_2$ separation", *Chem. Eng. J.* **479**, 147401 (2024)

Emerging Materials
Room Hall 3 - Session EM-TuP

Emerging Materials Poster Session

EM-TuP-1 Atomic Layer Memory Switching for Power-Efficient Neuromorphic Computing, *Hyunho Seok, S. Son, T. Kim,* Sungkyunkwan University, Republic of Korea

Brain-inspired parallel computing has been considered for the breakthrough of memory bottlenecks to meet the needs of simultaneously overflowing informative data. Numerous studies have been conducted on the development of reliable memristor arrays, energy-efficient computing, and various operational mechanisms for synaptic devices. However, for bioplausible neuromorphic computing, and temporal and spatial investigations as input signals toward leaky integrate-and-fire systems should be realized.

In this research, the importance of two-dimensioinal material based neuromorphic computing is addressed, and the basic components of the hardware neural network system are presented. Transition metal dichalcogenides (TMDCs) which is widely utilized for advanced van der Waals (vdW) based electronics is proper candidate for neuromorphic devices owing to atomically thin layered structure and superior electronic properties. Owing to the atomic structures, low-powered energy consumption can be realized.

Two-terminal devices of artificial and artificial synapses have been used as single components in neuromorphic computing, but they are associated with critical issues, such as current leakage and the absence of a third terminal as a fine synaptic weight modulator. To fully mimic biorealistic artificial neural networks, the integration of artificial neurons and synapses, hardware implementation of neurobiological functionality, and sensory neuromorphic computing are required. From single-component devices to architectures, the operational mechanism of each artificial component is unraveled, and the realization of bioplausible neuromorphic computing through integration is comprehensively discussed for future brain-inspired electronic systems.

EM-TuP-2 Electron-Enhanced Atomic Layer Deposition (EE-ALD) of TiCN Ternary Nitrides with Tunable Composition, *Z. Sobell,* **Michael Collings**, *S. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiCN ternary nitride films with tunable composition at T< 140°C.TiCN EE-ALD was performed using sequential exposures of tetrakis(dimethylamido) titanium (TDMAT) and electrons together with the continuous presence of an ammonia (NH_3) reactive background gas (RBG) (Figure 1). The electrons can remove surface species via electron stimulated desorption (ESD).NH_3 can also be dissociated by the electron beam to produce H and NH_x radicals. The NH_x radicals may facilitate Ti nitridation and C removal from the film (Figure 2). The C content of the TiCN films can be tuned by varying the electron beam exposure time or the NH_3 RBG pressure.

Reducing the electron beam exposure reduces the production of active NH_x species and allows more carbon incorporation into the films during TiCN EE-ALD.Electron exposures were varied from 0.5 to 20 seconds. Electron exposures of 0.5 s resulted in a C:Ti ratio of 1:4, while electron exposures of 20 s resulted in a C:Ti ratio of 1:28, as measured by ex situ XPS (Figure 3).The resistivity of the films determined by 4-wavelength in situ ellipsometry is also affected by the carbon content.Films grown with a 0.5 s electron exposure had a resistivity of ~800 μΩ cm.Films deposited with a 20 s electron exposure time had a resistivity of ~200 μΩ cm.

TiCN films can also be grown by reducing the NH_3 partial pressure during TiCN EE-ALD.Lower NH_3 partial pressures lead to fewer active NH_x species present in the reactor and allow for the incorporation of more C into the films. NH_3 pressures were varied from 0 to 3.3 mTorr.Both the C:Ti ratio and the resistivity of the films varied with NH_3 pressure.The C:Ti ratio varied from 2:1 at no NH_3 to 1:10 at 3.3 mTorr NH_3, as measured by ex situ XPS.The resistivity varied from ~1000 μΩ cm for no NH_3 pressure to ~200 μΩ cm at an NH_3 pressure of 3.3 mTorr.

The use of a RBG during EE-ALD allows for compositional tuning of thin films.For example, TiN or TiO_2 films can be grown using TDMAT together with either NH_3 or O_2 RBGs.Varying the electron exposure or RBG pressure can also be utilized to control the film composition.Growth of binary or ternary ALD films is straightforward because EE-ALD with RBGs relies only on simple, volatile, gas phase precursors.

EM-TuP-3 Low-Temperature Atomic-Molecular Layer Deposition of Air-Stable and Conformal Zn-Benzenedithiol Thin Films, *Anish Philip, T. Jussila,* Aalto University, Finland*; J. Obenlueneschloss, D. Zanders, F. Preischel,* Ruhr University Bochum, Germany*; J. Kinnunen,* Chipmetrics Ltd, Finland*; A. Devi,* Ruhr University Bochum, Germany*; M. Karppinen,* Aalto University, Finland

The atomic/molecular layer deposition (ALD/MLD) thin-film technique is strongly emerging as a unique designer's tool for exciting new functional metal-organic materials. Current research demonstrates that this method is effective even at low deposition temperatures and capable of producing thin films that are highly stable and conformal. Stability and conformality are critical requirements of today's 3D microelectronics and open vast potential for various industrial applications. In this context, we highlight the attractive characteristics of a new ALD/MLD process developed for Zn-organic thin films based on non-pyrophoric bis-3-(*N,N*-dimethylamino)propyl zinc [Zn(DMP)$_2$] and 1,4-benzene dithiol (BDT) precursors. This process yields air-stable Zn-BDT films with a notable growth rate of 4.5 Å/cycle at 60 °C. The reported process ability to produce highly conformal thin films was verified on lateral high-aspect-ratio (LHAR) test substrates.The Zn/S ratio (0.5) determined with RBS for a planar film was in alignment with the expected compositions. The depth-profile XPS analysis for a LHAR grown Zn-BDT film indicated a composition change along the cavity, which maybe arising from the different sticking coefficients of the precursors. The reported films were found to be electrically insulating and demonstrated remarkable stability under ambient conditions over extended storage periods, making them a promising candidate for barrier coating application in microelectronics. Also importantly, using state-of-the-art LHAR test structures we could demonstrate that by increasing the precursor pulse lengths it was possible to extend the essentially ideal film growth deep (PD=260 μm) into the high-aspect-ratio cavities (Figure 1).

EM-TuP-4 Tin Oxide-Organic Superlattices for Flexible Thermoelectric Applications by Atomic/Molecular Layer Deposition, *Mari Heikkinen,* Aalto University, Finland*; N. Huster, A. Devi,* Ruhr-University Bochum, Germany*; M. Karppinen,* Aalto University, Finland

Flexible thermoelectric (TE) heat-to-electricity conversion devices would be highly beneficial for wearable applications and also for any application in which the heat source is complex shape.[1] A TE device principle is simple, but it needs both n- and p-type semiconductor legs to function.

An efficient TE material should have simultaneously high electrical conductivity and low thermal conductivity, which is a challenge for conventional materials. The second challenge is that the currently employed inorganic TE materials are composed of heavy/rare/poisonous elements (Bi, Te, etc.), which are not environmentally sustainable. Simple metal oxides like ZnO are relevant material candidates, but their thermal conductivity is too high.

The combined atomic and molecular layer deposition (ALD/MLD) technique allows us to mix inorganic and organic precursor pulses in a sequential manner, thus enabling precise layer-engineered superlattice (SL) structures. In our previous works, we have deposited ZnO:organic SLs where monomolecular organic layers are embedded within nanoscale layers of the n-type ZnO semiconductor to block the phonon conduction at the resultant metal oxide/organic interfaces without affecting the electrical conductivity.[2] Organic layers also improve the flexibility of the film.

Here we present similar efforts for the yet-missing p-type semiconductor counterpart SnO. We use an amidinate-based tin(II) precursor which reacts well with water as the co-reactant under ALD conditions for the deposition of the SnO layers.[3] Thin films deposited at 220 °C results in phase pure SnO. Saturation for tin precursor happens at 12 s and for water at 2 s. The thickness of the films is measured by X-ray reflectivity (XRR) and the composition analyzed by Fourier-transform infrared spectroscopy (FTIR). For the organic component, we investigate various possibilities (hydroquinone, terephthalic acid, etc.); tentatively, terephthalic acid is found a promising organic component, as it has more oxidative character than e.g. hydroquinone.

References

[1] G. Marin, R. Funahashi & M. Karppinen, Textile-integrated ZnO-based thermoelectric device using atomic layer deposition, *Advanced Engineering Materials***22**, 2000535 (2020).

[2] R. Ghiyasi, M. Milich, J. Tomko, P.E. Hopkins & M. Karppinen,Organic-component dependent thermal conductivity reduction in ALD/MLD grown

ZnO:organic superlattice thin films, *Applied Physics Letters* **118**, 211903 (2021).

[3] N. Huster, R. Ghiyasi, D. Zanders, D. Rogalla, M. Karppinen & A. Devi, SnO deposition via water based ALD employing tin(II) formamidinate: precursor characterization and process development, *Dalton Transact* **51**, 14970 (2022).

EM-TuP-5 Low Temperature Plasma Synthesis of Layer controlled MoS₂ for Flexible AI Accelerator, *Sihoon Son, H. Seok, D. Lee, H. Choi, T. Kim,* Sungkyunkwan University (SKKU), Republic of Korea

The achievements in implementing flexible electronics, departing from rigid silicon-based hardware substrates, are accelerating the emergence of "electronic skin." Such flexible electronics are gaining attention as an attachable electronic augmentation ranging from patch-type medical diagnostic applications to, ultimately, enhanced replacement for actual skin.

The information processing in actual human skin entails a system that dynamically integrates sensory compliance, threshold adjustment, and other complex nervous system functions, rather than being a mere collection of simple sensors. To attach AI diagnostic systems to the skin or, further, to mimic such systems for electronic skin, it is essential to produce neuromorphic hardware on flexible substrates. However, existing synthesis methods for MoS2, a material capable of superior and stable neuromorphic operation, involve high-temperature processes, posing significant limitations on direct growth onto flexible substrates.

In this study, MoS2 was directly synthesized onto flexible substrates via low-temperature plasma to fabricate a synaptic array and perform vector multiplication, which forms the basis of AI computations. The successful execution of vector multiplication was enabled by the rich grain boundaries of the synthesized MoS2, providing a stable resistive switching filament path, and demonstrated the maintenance of such hardware functionality even under bending.

EM-TuP-6 Efficient Scaling of Ruthenium Thin Films by ALD for High-Volume Manufacturing, *Parmish Kaur, B. Eychenne, M. Kääriä, A. Sood,* Picosun Oy, Finland

Ruthenium (Ru) is highly regarded for its remarkable electrical conductivity, chemical stability, and catalytic activity, rendering it indispensable in electronic, energy, and catalysis applications. Nonetheless, the prohibitive cost associated with Ru precursor materials impedes its widespread utilization.

This study investigates the deposition of Ru films via Atomic Layer Deposition (ALD) to explore its potential for high-volume manufacturing. Employing batch processing of substrates enhances operational efficiency and cost-effectiveness. The Ru films demonstrate a growth per cycle (GPC) of 0.35 Å cy^−1 at 250 °C, with a density of 12.3 g/cm^3 and surface roughness below 0.7 nm. Electrical resistivity of all films falls below 15 μΩ cm, indicative of highly conductive films.

Grazing incidence X-ray diffraction (GI-XRD) analysis affirms the crystalline structure of the films as hexagonal P63/mmc metallic Ru, while scanning electron microscopy (SEM) underscores their excellent conformal coverage. Minimal impurity content, as evaluated through time-of-flight elastic recoil detection analysis (TOF-ERDA), is observed.

Scaling up the Ru deposition process yields a notable 14-fold enhancement in precursor efficiency, yielding films endowed with desirable physical properties. Thus, the exploration of Ru ALD not only tackles economic challenges but also paves the way for the integration of Ru-based materials into cutting-edge technologies, fostering innovation and progress across diverse domains.

References:

Aaltonen, T., Alén, P., Ritala, M. and Leskelä, M. (2003), Ruthenium Thin Films Grown by Atomic Layer Deposition. Chem. Vap. Deposition, 9: 45-49. https://doi.org/10.1002/cvde.200290007

EM-TuP-7 Luminescent Lanthanide-Organic Hybrid Materials by Atomic/Molecular Layer Deposition, *Melania Rogowska, P. Hansen, O. Nilsen,* University of Oslo, Norway

Trivalent lanthanide ions (Ln^{3+}) show attractive optical properties like luminescence emission from ultraviolet (UV) to visible and even near-infrared (NIR) range depending on the metal ion used. In addition, they can participate in a unique photon upconversion process that requires interaction between two or even more Ln^{3+} ions. Such Ln^{3+}-doped materials could be implemented in various applications including solar cells, lasers, sensors, and bioimaging. The Ln^{3+} ions suffer, however, from weak light absorption and therefore inefficient direct excitation. Moreover, pure lanthanide oxides often display a concentration quenching, and in a consequence a lack of luminescence. These problems can be overcome by coupling species like organic ligands that can participate in energy transfer processes. In this sensitized luminescence, light is absorbed by the organic ligand, and energy is transferred to Ln^{3+} ions where the luminescence is generated. Furthermore, the presence of organic ligands can provide the separation between Ln^{3+} ions to overcome the concentration quenching.

Molecular layer deposition (MLD) is a suitable tool to produce such luminescent organic-inorganic hybrid Ln^{3+}-based materials with ultrahigh precision. This technique allows for accurate composition, thickness, and conformality control on a nanometer scale, which is specifically important for potential applications of luminescent materials as thin films and coatings. In this work, hybrid thin films were deposited using the β-diketonate $Ln(thd)_3$ precursors as a Ln^{3+} source (such as Nd^{3+}, Eu^{3+}, Tb^{3+}, and Yb^{3+}), and various aromatic dicarboxylic acids as organic linkers (including 1,4-benzenedicarboxylic acid and 2,6-naphthalenedicarboxylic acid). In addition, lanthanide fluorides (LnF_3) were incorporated into the films forming multilayer nanocomposite structures with more than one Ln^{3+} component showing strong luminescence emission. The final goal of this work is to create multilayer upconverting luminescent Ln^{3+}-based materials.

EM-TuP-10 Structural and Electrical Properties of Ta-Doped TiO₂ Prepared by Supercycle Atomic Layer Deposition, *Iqtidar Wasif,* FHR Anlagenbau GmbH, Semiconductor Physics, Chemnitz University of Technology, Germany; *H. Bryja, A. Muhammad, S. Simon,* FHR Anlagenbau GmbH, Germany; *N. Balayeva,* Semiconductor Physics, Chemnitz University of Technology, Germany; *J. Barzola Quiquia, M. Reinfried,* FHR Anlagenbau GmbH, Germany; *D. Zahn,* Semiconductor Physics, Chemnitz University of Technology, Center for Materials, Architectures, and Integration of Nanomembranes (MAIN), Chemnitz University of Technology, Germany

TiO₂ has been intensively studied as a transparent conductive oxide and photoanode for photovoltaic and photocatalytic applications. The conductivity of TiO₂ can be improved by doping with group V elements such as Nb or Ta. However, effectively tailoring their properties by means of controlled doping amounts is challenging. Atomic layer deposition (ALD) offers an accurate tuning of the elemental composition by alternating binary ALD processes in a supercycle approach. This work aims at the supercycle deposition of Ta-doped TiO₂ by thermal ALD and the effect of doping and annealing conditions on the structural and electrical properties of Ta: TiO₂ thin films. Titanium (IV) isopropoxide (TTIP) and (tert.-Butylimido)-tris-(ethylmethylamido)-tantalum(V) (TBTEMTa) are used as titanium- and tantalum-precursors, respectively, and water as a co-reactant.For the characterization of the structural properties of the thin films, Raman spectroscopy and X-ray diffraction (XRD) are used. The elemental compositions of the films are characterized by X-ray photoelectron spectroscopy (XPS) and/or energy-dispersive X-ray spectroscopy (EDX). Finally, the electrical properties are investigated to study the effects of different doping concentrations. The results show that by using the supercycle atomic layer deposition we have successfully modified the electrical properties of TiO₂ by systematic doping with Ta, which makes it attractive for future applications.

EM-TuP-11 Molecular Layer Deposition of Ferrocene-Based Thin Films, *Justin Lomax,* University of Western Ontario, Canada; *E. Goodwin,* Carleton University, Canada; *J. Bentley, J. Bosso,* University of Western Ontario, Canada; *C. Crudden,* Queen's University, Canada; *S. Barry,* Carleton University, Canada; *P. Ragogna,* University of Western Ontario, Canada

Ferrocene is known for its stable and reversible redox properties which makes it a promising candidate for crafting precisely controlled redox-active layers *via* atomic layer deposition (ALD).[1,2] Current microelectronic manufacturing faces challenges with the inability to further scale to smaller features due to defects and edge placement errors with modern deposition techniques. This study explores the application of ferrocene-based precursors in selective vapor and solution deposition processes, aimed to

develop redox-active organic layers to act as molecular binary switches for storing memory. Our approach uses ferrocene-appended molecules to achieve well-defined, high-quality layers on targeted metal substrates (Au or Cu) while avoiding non-growth regions. Small molecule synthesis, evaluation of precursor suitability, and characterization of films using Thermogravimetric Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and Atomic Force Microscopy (AFM) techniques will be discussed.

(1) Ferrocene—Beauty and Function. *Organometallics***2013**, *32* (20), 5623–5625.

(2) Parsons, G. N.; Clark, R. D. Area-Selective Deposition: Fundamentals, Applications, and Future Outlook. *Chem. Mater.***2020**.

EM-TuP-13 Atomic-Layer Deposition Techniques to the Deposition and Post-Synthesis Modification of Metal-Organic Frameworks, *Catherine Marichy*, B. Gikonyo, S. De, A. Fateeva, C. Journet, laboratoire des multimatériaux et interfaces (LMI), France

Metal-organic frameworks (MOFs) are a class of crystalline materials composed of metal ions/clusters as nodes bridged by organic moieties. These materials often exhibit remarkably high accessible specific surface areas, uniform and tunable pore volumes, and chemical modularity.MOFs have been synthesized mainly as powder or single crystals. However, to integrate these hybrid materials into microelectronic, thin films are needed. Different solution-based approaches, like layer-by-layer deposition,[1] have been developed to grow MOF films but solvent contamination limits their applications like in electronics domains.[2] Atomic/molecular layer deposition (ALD/MLD) approaches therefore circumvent this challenge as solvent-free MOF films with good quality, uniformity, and conformality are grown. In our group, we use ALD techniques to (a) directly deposit MOF thin films on solid substrates and (b) modify bulk MOFs by post-synthesis modification to adjust their properties, providing new functionalities while preserving the network structure.

(a) First direct growth of Copper-based MOFs by ALD/MLD is presented. Paddle-wheel frameworks, as copper terephthalate (Cu-TPA) and MOFs based on electrochemical active ligands as porphyrines, are successfully deposited using a home-made reactor. The obtained films are characterized using ellipsometry, UV-Visible, and IR spectroscopies, powder X-ray diffraction and scanning electron microscopy.

(b) To modify MOFs, in particular to incorporate metal cation in their reactive sites, vapor-phase infiltration (VPI) is also employed.[5] Herein, post-synthesis modification of microporous porphyrin-based MOFs by VPI will be introduced Using pulses of a single precursor (diethylzinc or trimethylaluminium), isolated metallic entities are installed in the stable and microporous Zr(IV)-based porphyrinic MIL-173(Zr) bulk MOF. Indeed, two reactive sites are present: the porphyrin core (free base), and a phenolic group in the meta position of the linker. The structural characterizations and spectroscopic properties of the modified MOF are presented.

[1] Zhang & Chang, *Processes*, **8**, 377 (2020).

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EM-TuP-14 A New Step Towards Crystalline III/V Semiconductors by ALD, *Thilo Hepp*, Philipps Universität Marburg / Dockweiler Chemicals GmbH, Germany; *P. Ludewig*, Philipps-Universität Marburg / Dockweiler Chemicals GmbH, Germany; *O. Briel, J. Koch*, Dockweiler Chemicals GmbH, Germany; *K. Volz*, Philipps-Universität Marburg, Germany

The production of III/V semiconductors by Atomic Layer Deposition (ALD) faces significant obstacles that hinder their widespread application. The selection of suitable precursor materials proves challenging because they must react with III/V semiconductor surfaces in a self-limiting manner to meet the requirements of the ALD process [1]. Good results have been published using alkyl-silyl based precursors [2]. However, a crystalline structure has not been achieved, impacting the efficiency and reliability of the semiconductors. Crystalline semiconductors are important for electronic and optical applications.

In addition, the inadequate leak tightness of conventional ALD systems leads to high oxygen incorporation in the epitaxial layers, resulting in detrimental defects. Oxygen is a deep trap in the band gap of semiconductors that significantly reduce the lifetime of optical devices.

To overcome these obstacles, the Philipps-University Marburg and Dockweiler Chemicals collaborate jointly. The Philipps-University will use its extensive expertise in CVD processes to optimize processes and develop innovative techniques. For this purpose, a MOCVD system has been rebuilt by the Sempa Systems GmbH to enable processes in a leak-tight tool as required for deposition of high quality III/V semiconductors.

Dockweiler Chemicals will focus on developing tailored chemicals to enhance the properties of the deposited material, such as crystallinity. Through this collaboration between academic research and industrial innovation, we aim to jointly address the challenges of ALD-based III/V semiconductor manufacturing and open new perspectives for the semiconductor industry.

A promising material system to dive into ALD of III/V semiconductors is GaP, which is, for example, an ideal buffer layer for the deposition of compound semiconductors on silicon (Si) for various applications such as lasers on Si or tandem absorbers [3]. In particular, the nucleation of GaP on Si 300 mm (001) wafers requires a delicate process and is challenging to control using MOCVD. A self-limiting ALD process would inherently produce a uniform layer on arbitrarily large substrates. However, crystal quality of III/V semiconductors gown by ALD remain a challenge. First results using alkyl-silyl precursors will be compared with samples grown using standard MOCVD precursors in a close coupled shower head reactor.

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EM-TuP-15 Pushing the Boundaries: Advancing Resist Technology for Beyond EUV Lithography Application, *Dan Le, T. Chu*, University of Texas at Dallas; *W. Lee*, stony Brook University; *N. Tiwale*, Brookhaven National Laboratory; *J. Veyan, J. Kim, D. Kim, M. Lee*, University of Texas at Dallas; *C. Nam*, Stony Brook University/Brookhaven National Laboratory; *J. Kim*, University of Texas at Dallas

Besides extending EUV lithography (EUVL) technology by utilizing optic systems with numerical apertures exceeding 0.55 (higher-NA EUVL) or even surpassing 0.75 (hyper-NA EUVL), reducing lithography wavelength (λ) from 13.5 to 6.7 nm has been of interest to accommodate the extreme downscaling of device critical dimension [1]. Alongside advancements in light sources and optical systems, the adoption of novel resist platforms is an important key factor for the readiness of 6.7 nm-based technology due to a reduction in material sensitivity [2].

Herein, we investigate the potential of a Zn-based hybrid thin-film system that is synthesized via ALD analog as a part of the *dry* resist platform for beyond EUV (BEUV) lithography technology. The growth characteristics and material stability of Zn-based hybrid thin films are evaluated, with the highest growth rate observed at 75°C (Figure 1a). Upon being exposed to electrons with energy similar to those of photons at 6.7 nm wavelength (~180 eV), the Zn-based inorganic-organic hybrid thin films exhibited negative tone characteristics when developed using diluted KOH solution (Figure 1b). The low-energy electron beam lithography (EBL) will be employed to rapidly assess the material sensitivity, with height profiles obtained using an atomic force microscope (AFM). Furthermore, we extend our focus on understanding the chemical alternations of the Zn-based hybrid thin films when exposed to electrons with energy similar to or lower than those of BUEV photons. The experiment is conducted using our unique *in-situ* FTIR system equipped with an electron flood gun and a residual gas analyzer (RGA). The *in-operando* RGA spectrum (Figure 2) indicates H_2, H_2O, CO, and CO_2 as byproducts produced during the electron exposures. The crosslinked mechanisms of Zn-based inorganic organic hybrid thin films are elucidated through *in-situ* IR absorbance and *in-operando* RGA analysis. A comparison between Zn-based and Al-based hybrid thin film patterning characteristics will also be conducted. This study highlights the potential of novel metal-containing hybrid thin films as a part of the *dry* resist platform and offers valuable insight for the development of novel resist technology for beyond EUVL applications, thus contributing to the ongoing advancement of lithographic techniques.

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

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EM-TuP-16 Multistep Inorganic Synthesis of Redox-Active THz Phononic Structure, *Norifusa Satoh*, National Institute for Materials Science, Japan; *R. Gordon*, Harvard University

The logic of chemical synthesis (Nobel prize in Chemistry 1990) originally for organic molecules is nowadays observed in inorganic synthesis, especially for the latest electronic device, known as atomic layer deposition (ALD), selective-area deposition, and atomic layer etching. To extend the synthetic strategy toward synthesis of atomically precise dot supper-lattices which cannot be obtained by other methods like molecule beam epitaxy (Nobel prize in Physics 2000), we herein propose an oxide-based combination of ALD and atomically precise dot deposition [ref. 1-3], because we can expect the following four advantages: (1) the strong ionic covalent bonds of oxides keep high melting points even on nanoscale dots to maintain the atomically precise structure without protective ligands [ref. 2,4]; (2) ALD precursors easily chemi-adsorb on the bare surface of oxide dots; (3) the separated oxide dots due to the original organic spacers are conformally solvated by dielectric ALD oxides to show redox reactions as if in solution [ref. 5]; (4) the periods of phononic contrast between the oxide dots and amorphous ALD oxides matches the wavelength of THz phonon over room temperature, less than 1 nm, to confine heat conduction [ref. 6]. In this research, we first confirmed the linear thickness growth based on the number of super cycle, second demonstrated the redox response of oxide dot inside a flash memory structure [ref. 7], and finally evaluated the effect of ALD cycle on thermal conduction using the previous method [ref. 8]. These results suggest the multistep inorganic synthesis may be able to design a new type of electron-phonon interaction or coupling.

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EM-TuP-17 Modelling the Growth of Zincone ALD/MLD Hybrid Thin Films: A DFT Study, *Mario Mäkinen*, K. Laasonen, Aalto University, Finland

Purely inorganic, or organic thin films can be fabricated using either atomic or molecular layer deposition (ALD and MLD). By combining these two methods, one can fabricate hybrid thin films, which contain both organic and inorganic layers, and thus will drastically improve the applicability of the thin film technology. Even though this deposition method has been used extensively experimentally, the reaction paths occurring during the thin film deposition process are still widely unknown. Density functional theory (DFT) -based modeling answers this problem, as we can study the growth mechanisms of hybrid thin films on an atomic-level accuracy.

Hybrid thin films under investigation were studied using gas-phase and surface reaction models, of which examples are presented in Figure 1. The surface models consisted of two differently ethyl-saturated zinc oxide surfaces, which account for the imperfection of the thin film growth, and the adsorbing organic precursor 4-Aminophenol. The gas-phase models consisted of diethyl zinc and an organic molecule from a variety of aliphatic and aromatic compounds.

Modelling of the reaction pathways was conducted using the GPAW program. DFT was used with the PBE exchange and correlation functional. Van der Waals correction TS09 was used due to weak interactions caused by the ethyl ligands. All the reaction barriers were calculated using the nudged elastic band -method with a climbing image (CI-NEB).

4-Aminophenol reacts faster and more strongly with its hydroxyl than its amino group, which will dictate the alignment of 4-Aminophenol in the film structure. 4-Aminophenol adsorbed to the surface through physisorption, and after that, the hydrogen will migrate to ethyl ligand within a complicated branching reaction chain. This process, of which an example is illustrated in Figure 2, utilizes primarily a ligand exchange but also a dissociation reaction. The amount of ethyl ligands partaking in the growth reaction of the hybrid thin film was approximately 20 to 25 percent. Different macrostructures of these hybrid thin films were compared and the effect of oxygen on the growth reaction mechanisms was discovered.

Gas-phase models were utilized in the screening of over a dozen compounds to discover the relative reactivity of different functional groups present in aliphatic and aromatic organic precursors. Our results on both the reactivity and bond strength between different functional groups agree qualitatively with experimental results. Thus, this rapid screening process enables the feasibility prediction of the potential organic precursors, and it can be expanded to hundreds of precursors.

EM-TuP-19 Tuning the Diffusivity of DEZ During Vapor Phase Infiltration in Photopatternable Polyacrylates by Increasing the Polymer Network's Flexibility, *Lisanne Demelius, A. Coclite,* Graz University of Technology, Austria; *M. Losego,* Georgia Institute of Technology

The kinetics of vapor phase infiltration (VPI) can be very complex due to various operational factors and intrinsic properties affecting precursor sorption and diffusion. These factors include the precursor's vapor pressure, process temperature, precursor size, the density of reactive polymer groups, precursor-polymer reaction rates, and polymer free volume. Understanding the transport and reaction mechanisms is crucial for the successful optimization of VPI processes and their application to new precursor-polymer systems.

In this work, we investigate diethyl zinc (DEZ) infiltration into highly crosslinked polyacrylates, a class of materials that has not been previously studied for VPI. Our findings reveal that in such a densely crosslinked system, diffusion becomes the limiting factor. By copolymerizing trimethylolpropane triacrylate (TMPTA) with its ethoxylated counterpart (ETPTA), which has longer and more flexible side chains, we could significantly enhance DEZ diffusion, highlighting the role of polymer free volume in VPI kinetics. X-ray photoelrctron spectroscopy (XPS) depth profiles showed that while only partial Zn infiltration is achieved for a 200 nm homopolymer film of pTMPTA even after 50 h of DEZ exposure, adding 10 wt.% of ETPTA is enough to allow for full infiltration of the polymer layer. At 25 wt.% of ETPTA, the time required to achieve complete infiltration with DEZ is reduced to 15 h, and at 75 wt.% it is as short as 2 h. In a similar manner, reducing the UV polymerization time of the photopolymers and thus decreasing their crosslinking density also improves DEZ diffusion. The observed transport behavior is in good agreement with the theoretical reaction-diffusion model for VPI developed by Ren, McGuinness et al.[1].

The polyacrylate system studied in this work is of particular interest for VPI because its photopatternability opens new avenues for the creation of hybrid organic-inorganic nano- and microstructures by integrating VPI with existing polymer patterning techniques. As a proof of concept, we demonstrate the selective DEZ infiltration of a photolithographically patterned p(TMPTA-c-ETPTA) copolymer film on poly (methyl methacrylate) (pMMA). Energy-dispersive X-ray spectroscopy (EDX) elemental mapping and XPS depth profiles confirmed that Zn was present only in the patterned copolymer structures, but not in the poorly infiltrating pMMA.

Overall, our findings advance the understanding of VPI process kinetics, and lay an important foundation for applying VPI to highly crosslinked polyacrylates for top-down property modification of photopatternable polymer structures.

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EM-TuP-20 Tailoring Pore Size and Surface Hydrophilicity in Ceramic Membranes: The Case of MLD-Grown Titanicone Layers, *Harpreet Sondhi, A. Nijmeijer,* Inorganic Membranes, University of Twente, Netherlands; *A. Kovalgin,* Integrated Devices and Systems, University of Twente, Netherlands; *F. Roozeboom,* University of Twente and Carbyon B.V., Netherlands; *M. Luiten-Olieman,* Inorganic Membranes, University of Twente, Netherlands

Membranes are used at large scale to purify surface or wastewater and are increasingly applied in nanofiltration (pore size range 1-10 nm) of organic solvents. However, mass organic solvent streams containing small molecules are still treated with traditional energy-intensive technologies like distillation. Here, polymeric membranes suffer from swelling, which can change pore sizes significantly due to solvent-membrane interaction. In contrast, ceramic membranes are hydrophilic and thus more robust yet challenging to reproduce commercially. In this study we have used Molecular Layer Deposition (MLD) to modify high-porosity Al_2O_3-based ceramic membranes with average pore size of 20 nm, by coating their internal surface with hybrid layers grown by MLD. Objectives were to 1) narrow the membranes' pore size and pore size distribution by depositing a TiO_2 layer (acting as an intermediate) from $TiCl_4$ and EG (ethane-1,2-diol). 2) To investigate the hydrophilicity of hybrid layers grown by MLD from $TiCl_4$ and three different organic co-reactants, being heptanol, 3-aminopropyltriethoxysilane (APTES), and n-phenyltrimethoxy-silane (n-PTMS). Depositions were carried out at temperatures ranging from 100 to 200 °C, pulse times ranging from 0.1 to 0.4 sec for $TiCl_4$, 1 to 20 sec for the co-reactants, and 60 to 120 sec for N_2 purging. Typically, using MLD, the

average pore size of the bare ceramic support (≈20 nm) could be reduced below 2 nm, as determined by permporometry, for 10 nm TiO_2 layer, see Fig. 1. The three hybrid layer types were also grown with identical process recipes on planar silicon substrates. This way, they could be tested on their surface hydrophilicity and chemical stability in different solvents (see Fig. 2),

1. Surface hydrophilicity was measured by way of measuring the respective Water Contact Angle (WCA). These WCA values were 109° (heptanol), 106° (APTES), and 114° (n-PTMS).
2. Chemical stability was measured by immersing the samples in solvents with decreasing polarity: water > acetone > ethyl acetate > hexane. The n-PTMS-based hybrid layer showed the most promising results:exhibiting excellent stability against hexane (non-polar), without layer degradation or change in its wetting performance (WCA constant at 114° after 24 hrs and seven days). While the heptanol- and APTES-based layers reacting with solvents lost hydrophobicity (WCA reducing to < 90°).

The results obtained so far provide new insights into the effect of using different organic co-reactants in MLD to optimize pore size and surface hydrophilicity to improve ceramic membranes' performance in organic solvent nanofiltration.

EM-TuP-21 Flexible Conductive Hybrid: Indium Oxide-ParyleneC Obtained by Optimized Vapor Phase Infiltration, *Oksana Yurkevich,* CIC NanoGUNE, Spain*; E. Modin,* CIC nanoGUNE, Spain*; I. Šarić Janković, R. Peter, M. Petravić,* Department of Physics and Centre for Micro- and Nanosciences and Technologies University of Rijeka, Croatia*; M. Knez,* CIC nanoGUNE, IKERBASQUE Basque Foundation for Science, Department of Physics and Centre for Micro- and Nanosciences and Technologies University of Rijeka, Spain

The advancement in enhancing traditional organic or inorganic materials has reached a plateau, necessitating a significant step forward by concurrently exploiting the properties of both organic and inorganic materials. Over the last decade, vapor phase infiltration (VPI) has gained substantial attention as a versatile top-down approach for crafting hybrid materials. Various hybrid systems, incorporating a blend of metal oxide and polymer, have been developed. Of particular interest is In_2O_3, an essential component in materials employed for transparent electrodes such as indium tin oxide or indium zinc oxide, pivotal for the electronics industry.

Our research focuses on the creation of a hybrid material based on indium oxide and Parylene C and further polymers of technological relevance. The polymer in our approach serves as a dielectric and flexible polymeric matrix. To gain a deeper understanding of this hybrid material system, we examine the impact of the oxygen source on VPI of indium oxide into Parylene C using trimethylindium (TMIn) and three distinct oxygen-containing precursors, water (H_2O), hydrogen peroxide (H_2O_2) and ozone (O_3). Through the application of these processes to the polymer, we analyze the hybrid Parylene C/In_xO_y samples by transmission electron microscopy (TEM), depth-profiling with secondary ion mass spectrometry (SIMS), and X-ray photoelectron spectrometry (XPS). The study contrasts the differences between the various precursor combinations.

Our findings reveal that employing hydrogen peroxide as the second precursor in a TMIn-based VPI process is advantageous compared to using water. The reactivity of H_2O_2 contributes to higher growth rates, deeper infiltration, and lower onset temperatures for crystallite formation of indium oxide in the TMIn/H_2O_2 process compared to TMIn/H_2O, while ozone degraded the polymer chains and a lowered its mechanical flexibility, limiting the applicability of TMIn/O_3 process. The resulting hybrids are conductive and exhibit sheet resistance values as low as 3 kΩ/□ without additional annealing. Furthermore, these hybrids display a surprising ability to heal ruptures and defects in the conductive layers on their surface. Given that Parylene C is a dielectric and indium oxide is a wide band gap semiconductor, the amalgamated flexible conductive hybrids hold great promise for applications in electronics, such as flexible electrodes in wearables, displays, solar cells, or medical sensors.

EM-TuP-22 ALD Ternary Films and Nanolaminates Based on Al_2O_3, ZrO_2 and ZnO, *Piotr Polak,* J. Jankowska-Śliwińska, L. Stańco, J. Maleszyk, A. Łaszcz, Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland*; A. Wolska, M. Klepka, K. Jabłońska,* Institute of Physics, Polish Academy of Sciences, Poland*; H. Stadler,* Bruker Nano Surfaces, Germany*; K. Kosiel,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

Metal oxide nanocoatings show strong application potential in many areas including anti-corrosion protection, surface engineering of polymers, medical materials, or electrode/electrolyte interfaces in all-solid-state batteries, to name just a few. Precise tuning of the functional properties of coatings, however, creates the need to fabricate materials that are more complex than binary ones. ALD is an excellent tool for fabrication such conformal multi-component thin-film coatings, enabling strict control of their thickness and composition or doping profiles. However, the ALD of such complex layers is usually far from satisfying the rule of mixtures and does not provide a linear dependence for growth-per-cycle and composition on the relevant parameters specific to the growth of binary materials. Therefore, surface engineering using multi-component ALD oxides requires in-depth experimental knowledge on layer growth using various substrates.

For our research we used ALD Beneq TFS-200 equipment. We experimentally tested thermal ALD of Al_2O_3, ZrO_2 and ZnO thin films, as well as their mixtures (three different ternaries) and nanolaminates. For deposition of complex films we used a supercycle approach. The processes temperature range was 100-300°C. The films were generally only several tens of nanometers thick, and most were less than 20 nm. Silicon and gallium arsenide were used as substrates. We used trimethylaluminium, tetrakis(ethylmethylamino)zirconium (IV) and diethylzinc as chemical precursors for Al, Zr and Zn, respectively. We alternatively used deionized water or ozone as oxygen precursors. We proved the possibility of controlling the thickness and composition, though they typically deviated from the properties expected by the rule of mixtures. Thickness and composition of the films were analysed by a combination of spectroscopic ellipsometry, transmission electron microscopy energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. For selected films we analysed also coating tightness, surface topography and electrical properties using atomic force microscopy (by tapping mode and conductive AFM).

EM-TuP-24 Thin Film Composite Desalination Membranes by Molecular Layer Deposition, *Brian Welch,* R. Cai, Technion Israel Institute of Technology, Israel*; V. Rozyyev, J. Elam,* Argonne National Laboratory, USA*; T. Segal-Peretz,* Technion Israel Institute of Technology, Israel

The conventional preparation of thin film composite (TFC) reverse osmosis membranes involves interfacial polymerization (IP) atop a porous, polymeric support. This process can create selective polyamide films 100+ nm thick, with complex, yet relatively inhomogeneous morphologies. While commercially successful, IP is limited in its ability to control the selective layer composition, thickness and morphology which hinders transport properties and operational lifetime.

To overcome the limitations, we have developed TFC reverse osmosis membranes using all-organic molecular layer deposition (MLD) rather than IP. Key to fabrication was the ability to grow the MLD film across the pore openings of a porous substrate despite the conformal nature of MLD. To do so, we developed a sacrificial polyvinyl alcohol (PVA) pore filling process that enabled growth atop porous polyethersulfone supports while avoiding undesirable infiltration effects. Selective polyamide MLD films were made from m-phenylenediamine and trimesoyl chloride precursors at 3 Å/cy, 120°C. Vapor phase infiltration of the organic precursors into the PVA was investigated with in-situ ellipsometry. In crossflow desalination tests, MLD TFC membranes had improved water flux and NaCl rejection compared to commercial IP membranes. Improvements in performance were attributed to differences in the synthesized materials: compared to IP, MLD films were dense, highly crosslinked, and morphologically conformal, without nanoscale voids. Furthermore, a tradeoff between flux and salt rejection could be tuned by varying the thickness and composition of the MLD

selective layer. This research has broad implications for this and other applications which use TFCs, such as gas separations and nanofiltration.

EM-TuP-25 Complex Materials for Next Generation Electronics and Photonics - ALD will Prevail!, *Henrik H. Sønsteby,* University of Oslo, Norway

Even though semiconductor industry is doing a great job in tearing down scaling walls to increase the longevity of traditional Si-technology, new materials solutions are inevitably needed to harness the greatness promised by future ICT. This includes true edge computing for the ultra-connected smart society, as well as novel devices for neuromorphic computing. It is only natural that different technologies and device architectures are developed for different use - and with this more dedicated materials solutions for different applications.

These new materials will still need to adhere to many of the same processing constraints that we know from Si-ICT, such as low thermal budget, extreme conformality and thickness control - making ALD the most (if not the only) viable synthesis technique also as we look towards the next generations.

In this work we present how we are purposefully crafting an ALD catalogue of complex oxides with a wide range of functional properties. This includes materials that exhibit ferromagnetic, ferroelectric, metallic and semiconducting behavior, as well as combinations of these functionalities. We show how the quirks of ALD-processes and precursors can be exploited to enable low-temperature epitaxy of these materials. We point at cation substitution with high compositional control, strain engineering by careful choice of substrate and strategic process design to enable high quality crystal growth.

Materials such as $RENiO_3$ (RE = La - Lu), $BaTiO_3$, $NiFe_2O_4$ and $BaSnO_3$ are used as examples of materials with different functionalities, and where distinct ALD process design is needed to facilitate crystal growth. We introduce some ideas that aid ALD process design for complex oxides - letting us quickly tune in to optimal conditions.

We strongly advocate for the pivotal role of ALD in advancing ICT through the utilization of dedicated materials for emerging technology paradigms. However, this expansion imposes new challenges on ALD process development, necessitating innovative solutions. Through this work, we address these challenges and propose strategies to overcome them.

EM-TuP-26 Nanomolecularly-Induced Effects on the Synthesis and Stability of Multilayered Titania/Organophosphonate Interfaces, *C. Rowe,* Rensselaer Polytechnic Institute*; A. Kashyap,* Indian Institute of Technology, Mandi, India*; G. Sharma,* Rensselaer Polytechnic Institute*; N. Goyal,* Indian Institute of Science, Bangalore, India*; J. Alauzun,* University of Montpellier, France*; S. Barry,* Carleton University, Canada*; N. Ravishankar,* Indian Institute of Science, Bangalore, India*; A. Soni,* Indian Institute of Technology, Mandi, India*; P. Eklund, H. Pedersen,* Linköping University, Sweden*; **Ganpati Ramanath,** Rensselaer Polytechnic Institute

Nanoscale hybrid inorganic-organic multilayers are attractive for accessing emergent phenomena and properties through superposition of nanomolecularly-induced interface effects. Here, we demonstrate the effects of interfacial molecular nanolayers (MNLs) of organo-diphosphonates on the growth and stability of titania nanolayers during the synthesis of titania/MNL multilayers by sequential atomic layer deposition and single molecular layer deposition pulses. Electron microscopy, X-ray reflectometry and Rutherford backscattering spectrometry reveal that interfacial organo-diphosphonate MNLs result in ~20-40% slower growth of amorphous titania nanolayers than those grown at identical conditions without MNLs. The MNLs also inhibit anatase nanocrystal formation from the amorphous titania nanolayers. Both effects are more pronounced in multilayers with aliphatic-backbone-MNLs than those with aromatic-backbone-MNLs. Elastic recoil spectroscopy analyses reveal a MNL-induced increase in impurity incorporation from the titanium precursor. These results collectively suggest MNL-induced diminution of growth kinetics and suppression of nanocrystal formation are likely due to incomplete and/or altered surface reactions. Both aliphatic- and aromatic-backbone MNLs result in twofold higher film roughness, suggesting that roughening is primarily due to MNL bonding chemistry. Such MNL-induced effects on inorganic nanolayer growth rate, roughening and stability are germane to realizing high-interface-fraction hybrid organic-inorganic nanolaminate multilayers.

EM-TuP-27 Comparative Analysis of Film Growth in Molecular Layer Deposition: Siloxane-Bridged Silane Precursor vs. Methylene-Bridged Silane Precursor, *Man Hou Vong, M. Dickey, G. Parsons,* North Carolina State University

Molecular layer deposition (MLD) of siloxane-based polymers can be highly useful because these polymers (for example, polydimethylsiloxane) have vast applications in different fields. However, previous literature reported that MLD of siloxane-based polymer using homo-bifunctional siloxane-bridged silane molecules was ineffective due to the lack of film growth.[1] In this work, the growth of siloxane-based polymers in MLD using siloxane-bridged (Si-O-Si) silane precursor and water was investigated and compared to the growth of carbosilane-siloxane film using methylene-bridged (Si-CH_2-Si) silane precursor and water. Our results show that the film deposited with methylene-bridge precursor can grow beyond 1 nm whereas the film deposited with siloxane-bridged ultimately stops growing after the film thickness reaches only a few angstroms. This finding suggests that the rigidity of the bond angle between the functional groups may play a role in mitigating the occurrence of "double reaction" – that is, the functional groups on both ends of the precursor react with the surface of the substrate – which results in promoting film growth. The findings reported in this work also provide insights into the growth mechanism of ultra-thin organic thin films.

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EM-TuP-30 Physical, Chemical and Architectural Metal-Ceramic Nanolaminate Design for Enhanced Mechanical Properties, *A. Sharma,* Swiss Cluster AG, Switzerland*; S. Tsianikas, J. Michler, X. Maeder,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; **Carlos Guerra-Nuñez,** Swiss Cluster, AG, Switzerland

Metal multilayer composites can show an enhancement of both strength and ductility related to the structure and properties of the interfaces between the layers, as well as the thicknesses and properties of the individual layers [1-2]. However, nanolaminate structures often suffer microstructural instability during annealing and extreme deformation conditions. It is well known that the alloying addition in bulk nanocrystalline materials can significantly improve the microstructural stability and mechanical properties by grain boundary pinning, secondary phase precipitation and other segregation related mechanisms. Although there is ample literature available on the mechanical behaviour of pure metallic nanolaminate structures, the experimental results of the effect of alloying addition on the microstructural stability and mechanical properties in the metal nanolaminated structures is rather limited.

Here, we present recent experimental data on the fabrication and mechanical behavior of nanolaminate FCC-BCC high entropy alloy thin films with interlayer thickness 50 nm and Cu-Al thin films with interlayer thickness 30, 50 and 120 nm.The layers are separated by atomic layer deposition of 2 nm amorphous Al_2O_3 layer without breaking the vacuum in a new Cluster System combining both ALD and PVD in the same equipment (Swiss Cluster AG). As a model system, FCC-NiCoCrFe and BCC- NiCoCrFe-Al (with Al ~20 at. %) and $Cu_{1-x} – Al_x$ (X: 0, 5 and 10 at.%) layers with a total thickness of 3 microns is deposited on Si (100) substrate by magnetron sputtering and subsequently tested by micro compression experiments. The mechanical response of the multi-layered structures is also compared with single-layer counterparts. It is observed that presence of ALD layers significantly improves the strength and ductility in the films. Moreover, the multilayered microstructure takes advantage of multiple small-scale mechanisms such as Hall-Petch, solid solution, and Orowan precipitate strengthening for enhanced mechanical properties compared to bulk. The post-mortem electron microscopy investigation provides insight into deformation mechanisms in the individual layers.

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Emerging Materials
Room Hall 3E - Session EM-WeM

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

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

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

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

Here we obtain through ALD/MLD in-situ crystalline, air-stable Fe-BDC thin films different from the Fe-BDC MOFs prepared in bulk form.[4] These thin films are characterized with a combination of advanced experimental and computational methods such as synchrotron grazing-incidence X-ray diffraction (GIXRD) and resonant inelastic X-ray scattering (RIXS) to disclose their unique chemical and structural features. The investigations reveal the existence of both Fe(III) and Fe(II) in the films and, excitingly, converge towards a novel crystalline Fe(III)-BDC phase with space group $C2/c$ (Figure 1), and a previously unknown amorphous Fe(II)-BDC phase. Resolving the structure of a thin film material can be exceedingly demanding for materials with no bulk counterparts to compare with as traditional methods such as Rietveld refinement cannot be realized for thin films; this work provides a valuable example how the novel structures can be nevertheless determined.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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Wednesday Afternoon, August 7, 2024

Emerging Materials
Room Hall 3E - Session EM-WeA

Other Emerging Materials

Moderators: **Jiyoung Kim**, University of Texas at Dallas, **Mato Knez**, CIC nanoGUNE

1:30pm EM-WeA-1 Atomic-Scale Homogeneous PtRu Alloy Thin Films Prepared by Atomic Layer Modulation (ALM), *Yeseul Son, S. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea; *T. Cheon,* Daegu Gyeongbuk Institute of Science and Technology, Republic of Korea; *S. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea

To create multi-component thin films with ALD, the super-cycle method is commonly used. By adjusting the cycle for each ALD process of each material to be mixed at an appropriate ratio, it is possible to produce a thin film with an arbitrary element ratio. However, the distribution of elements in the depth (thickness) direction is non-uniform or forming nano-laminate structure, and to obtain the composition of the desired ratio, it is necessary to produce a thin film of at least several nm. In this study, to address this problem, a newly proposed atomic layer modulation technology (ALM) [1] was used. ALM technology enables the production of uniform multi-component thin films at the atomic layer level by sequentially exposing multiple precursors within one cycle [Fig. 1]. So, atomic-scale homogeneous alloy films of Pt, which is highly active in hydrogenation reactions and has a bulk resistivity of 10.6 $\mu\Omega$ cm and work function of 4.71 eV, and Ru, which is highly active in oxygenation reactions and has a bulk resistivity of 7.1 $\mu\Omega$ cm and work function of 5.65 eV, was successfully prepared [Fig. 2]. Here, metal-organic precursors, tricarbonyl(trimethylenemethane)ruthenium [Ru(TMM)(CO)$_3$] and dimethyl-(N,N-dimethyl-3-butene-1-amine-N)platinum (C$_8$H$_{19}$NPt) were used and a self-limiting growth for each Ru and Pt ALD, was confirmed. By controlling the condition of ALM process, we can prepare ALM PtRu alloy thin films with different compositions and their properties with the composition were systematically analyzed by SIMS, TEM, XPS, XRD, XRR etc. The performance of ALM PtRu alloy film as a wiring material to replace Cu as well as a catalyst for HER (hydrogen evolution reaction) and OER (oxygen evolution reaction) will be presented in the conference.

*Corresponding Author: soohyunsq@unist.ac.kr

[1] Nguyen, C. T., et al., "Atomic Layer Modulation of Multicomponent Thin Films through Combination of Experimental and Theoretical Approaches", Chem. Mater. 2021, 33, 4435−4444.

1:45pm EM-WeA-2 A New Approach to the Synthesis of Nb@TiO$_2$ Core-Shell Composite for Oxide Dispersion Strengthened Alloy via Atomic Layer Deposition, *Ji Young Park, E. Lee, M. Jeong, J. Byun, B. Hwang, S. Oh, B. Choi,* Seoul National University of Science and Technology, Republic of Korea

More than half of CO$_2$ emissions in the world come from fossil fuels; therefore, in order to significantly reduce them, it is necessary to develop efficient internal combustion engines. In an attempt to enhance their mechanical properties in extreme conditions, it is required to have high thermal stability and strength as well as high durability and corrosive resistance. Nowadays, many types of research (alloying, surface and heat treatments, etc.) have been conducted to develop eligible refractory materials.

Nano-oxide dispersion strengthened (ODS) refractory alloy has been attracting attention because of its outstanding mechanical reinforcement mechanism. Dispersed oxides enhance the strength by preventing grain growth and recrystallization as well as increasing creep resistance, which allows ODS to be widely applied in extreme fields such as military industries and aerospace. ODS alloys are commonly fabricated by mechanical alloying methods. However, it can draw impurities and cracks in raw powders, which influence on porosity of pellets. In this research, atomic layer deposition (ALD) is applied to synthesize ODS alloy. ALD is one of the most promising technologies in thin film deposition. It is useful to coat conformal thin films even on complex shapes of matrix such as nanorods or powders without mechanical damage. We coat pure Nb powder with TiO$_2$ thin film by using rotary-reactor type thermal ALD. TiO$_2$ chosen as the coating layer is non-toxic and chemically stable in high temperatures. In addition, it has superior mechanical strength as well as anti-wear and corrosion properties, thus widely adopted to ODS. TiO$_2$ is grown by using Titanium tetraisopropoxide (TTIP) precursor and H$_2$O reactant gas at 200°C. Transmission electron microscopy analysis reveals that TiO$_2$ is deposited uniformly on the Nb powder and the thin film in pellets is dispersed to be crystallized. Spark plasma sintering method is applied for sintering powders to minimize residual stress and grain coarsening. Thin film analysis including X-ray photoelectron spectroscopy and X-ray diffraction is conducted to understand the physical and chemical properties of the coating layer and its matrix. Grains with grain boundaries in pellets are analyzed via electron backscatter diffraction method. Mechanical properties are investigated by Vickers hardness test and nanoindentation measurement to confirm the TiO$_2$ dispersion strengthening effect on Nb refractory matrix. This study proposes a new field of ALD. This technology can be further applied to the surface and interface engineering of powder materials for electronic and energy applications.

2:00pm EM-WeA-3 Influence of an Artificial Structure on the Mechanical Properties of Atomic Layer Deposited Al$_2$O$_3$ and Ta$_2$O$_5$ Composite Thin Films, *Helle-Mai Piirsoo, T. Jõgiaas, K. Kukli,* University of Tartu, Estonia

The functionality of nanodevices depends on the mechanical reliability of their components like thin films. It has been shown that atomic layer deposited oxides in a periodic layered architecture possess lower residual tensile stresses [1], higher hardness [2], better wear properties [3] compared to their single constituents. ALD-grown nanocomposite thin films can improve the mechanical resistance of nanodevices.

In this work, amorphous Al$_2$O$_3$ and Ta$_2$O$_5$ thin films, their nanolaminates and mixtures were atomic layer deposited to thicknesses of ~70 nm. The single constituent layer thickness in multilayers, consisting of equal amounts of Al$_2$O$_3$ and Ta$_2$O$_5$, was varied from 18 to 1 nm. Trilayers with varying oxide volume fractions were deposited. The films were annealed at 800 °C for 10 min in air.

The amorphous reference Al$_2$O$_3$ film was harder compared to reference Ta$_2$O$_5$ by ~3 GPa and possessed ~15 GPa higher Young's modulus [4]. The hardness did not vary with the single layer thickness of amorphous nanolaminates, while mixtures were slightly harder compared to the laminates (Fig. 1). The elastic modulus decreased below that of the references in some multilayers (Fig. 2).

Annealing promoted the formation of orthorhombic Ta$_2$O$_5$ phase in the reference film [5] and in some composites. The Al$_2$O$_3$ film remained amorphous. The single constituent layer thickness had an influence on the hardness in nanolaminates with crystallized Ta$_2$O$_5$ layers. Nanolaminates with constituent layer thickness below 12 nm remained X-ray amorphous and softer compared to the crystalline nanolaminates and mixtures (Fig.1). The elastic modulus was modified with annealing for some of the multilayers (Fig.2).

The architecture of the trilayers affected hardness more than the Al$_2$O$_3$/Ta$_2$O$_5$ volume ratio, while the modulus of elasticity increased with increasing Al$_2$O$_3$ content after annealing.

The results show a possibility of engineering the mechanical properties of ALD thin films.

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2:15pm EM-WeA-4 ALD Young Investigator Award Finalist Talk: Phosphorus-Rich Metal Phosphide Thin Films Using Zintl Ions, *Jordan Bentley,* University of Western Ontario, Canada; *B. van Ijzendoorn,* Manchester Metropolitan University, UK; *J. Lomax,* University of Western Ontario, Canada; *M. Bakiro, S. Barry,* Carleton University, Canada; *M. Mehta,* Manchester Metropolitan University, UK; *P. Ragogna,* University of Western Ontario, Canada

Metal phosphide thin films can be prepared by vapour deposition techniques using various metal and phosphorus precursor combinations.[1] The resulting materials have applications in microelectronics, catalysis, and energy storage. For example, transition metal analogues such as FeP, CoP, and NiP, are effective catalysts in hydrogen evolution reactions or as

electrode materials for Li-ion batteries.[2,3]As for main-group metals, group 13 and 14 congeners such as GaP, InP, and GeP possess bandgaps that are amenable to photovoltaic and transistor applications.[4] Metal phosphides usually require organophosphorus or PH_3 as the phosphorus source, but here, we demonstrate that the heptaphosphide cluster (P_7^{3-}) can serve as an effective phosphorus precursor for making thin films by molecular layer deposition.[5] This opens a pathway to phosphorus-rich metal phosphide thin films (MP_2, MP_3, MP_4) which can exhibit superior properties to binary metal phosphides in some cases. [6] We used a specially designed crossflow vapour deposition system and then annealed the films to achieve uniformity. To the best of our knowledge, this is the first time that main group clusters were employed in vapour deposition. This opens up the possibility of creating novel materials with tailored properties at the nanoscale level. Current data supports that $P_7(SiMe_3)_3$ is sufficiently robust up to ~250 $^{\circ}C$ as measured by DSC and can be volatilized. A volatilization temperature under 1 torr (T_v) was estimated to be ~130 $^{\circ}C$; isothermal data at 130 $^{\circ}C$ and 150 $^{\circ}C$ support the linear mass loss of $P_7(SiMe_3)_3$ over 2 hours. We will present details on the precursor, thin film preparation, and analyses such as powder X-ray diffraction, electron dispersive spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and quartz crystal microbalance.

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2:30pm EM-WeA-5 Improved Crystallinity and Polarity Determination of Gallium Nitride on Si (111) Using Atomic Layer Annealing, *S. Yun, Ping-Che Lee,* University of California San Diego*; A. Mcleod,* University of California at San Diego*; J. Spiegelman,* RASIRC*; A. Kummel,* University of California at San Diego

The crystallinity and polarity of III-V semiconductors are critical for the passivation layers on microLED, the formation of 2D electron gasses in high electron mobility transistors, and for templating growth of piezoelectric materials. The atomic layer annealing (ALA) was reported to improve the crystallinity of the III-V compounds (aluminum nitride) at low temperatures as compared to the conventional thermal ALD. In ALA, a pulse of ion bombardment is added to each ALD cycle to ensure polycrystalline film formation at low temperature. Polycrystalline GaN has been deposited by ALA at low temperatures even on amorphous substrates, but polarity was not reported.

Figure 1a and 1b show the process parameter switching diagram for the GaN thermal ALD and GaN ALA processes, respectively. For GaN, tris(dimethylamido)gallium(III) (Strem Chemicals) and N_2H_4 (Rasirc) were used as precursors. The chemical compositions of GaN ALDs/Si were estimated by *in-situ* AES as shown in Figure 1c. Lower O contents (below 3.3 at. %) and higher N/Ga atomic ratio were observed in the ALA GaN on Si (111) as compared to the thermal ALD GaN film (4.6 at. %). Figure 1d shows that the intensity of GaN (002) XRD pattern in thermal ALD GaN on Si was greatly improved in the GaN stacks (GaN thermal ALD/ALA/Si) with an ALA GaN buffer layer.

Figure 2a and 2b shows the HAADF-STEM images of GaN ALDs/Si demonstrate highly ordered 3 nm × 5 nm ALD GaN layers. The circles of bright regions and the center of dark regions represent Ga atoms and tunnel points (empty element), respectively. The GaN polarity could be determined by drawing triangles connecting adjacent three tunnel points without the interruption of Ga. Using this method, upward triangles were obtained in the Figure 2a, suggesting the formation of N-polar GaN layers during the ALA GaN process on Si. Conversely, downward triangles from the STEM image of thermal ALD GaN/ALA/Si (Figure 2b) suggested Ga-polar GaN during GaN thermal ALD process. The inset figures show the top-view SEM image of selectively wet-etched (30 min, 20 wt.% KOH(aq)) GaN films. The etched surface on the ALA GaN (inset of Figure 2a) indicated N-polar GaN surface. The inset SEM image in Figure 2b shows a nearly unchanged GaN surface in thermal ALD GaN/ALA/Si is consistent with the Ga-polar GaN

surface. These observations are in good agreement with the HAADF-STEM images.

The data is consistent with being able to control the polarity of GaN by switching between thermal ALD and ALA. The ion bombardment in ALA promotes N-polar GaN while thermal ALD promotes metal polar GaN. This allows the facile formation of both electron and hole gas layers between ALA and ALD GaN.

2:45pm EM-WeA-6 Self-limiting Epitaxy of GaN and InN Films on Sapphire Substrates, *S. Allaby, N. Ibrahimli, F. Bayansal, H. Saleh, B. Willis, **Necmi BIYIKLI,*** University of Connecticut

Research efforts on low-temperature (T < 300 $^{\circ}C$) synthesis of crystalline III-Nitride 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 oxide-free stainless-steel based hollow-cathode plasma (HCP) sources revealed highly (002) oriented polycrystalline GaN films on Si(100) and sapphire substrates. In this work, we share our experimental findings on the self-limiting growth of GaN and InN films on sapphire substrates using HCP-ALD at 200 $^{\circ}C$ substrate temperature, revealing (002) oriented hexagonal monocrystalline layers.

The films were deposited using conventional metal-alkyl precursors (triethylgallium, trimethylindium) and various nitrogen plasmas (N_2/H_2, N_2-only, N_2/Ar, and $N_2/H_2/Ar$) as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed at 200 °C substrate temperature and a mild 100 W rf-power. *In-situ* Ar-plasma annealing cycles were also employed and tested for the binary III-nitride films to observe its impact on the surface crystallization process. *In-situ* ellipsometry was employed to monitor the surface ligand-exchange reactions and plasma surface interactions, in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness variation, growth-per-cycle (GPC), and optical properties of the III-nitride films.

When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for III-nitride films on c-plane sapphire substrates showed a notable increase. Grazing-incidence XRD (GIXRD) measurements revealed single-phase hexagonal polycrystalline GaN and InN films on Si(100) substrates while GaN/sapphire and InN/sapphire film samples exhibited substantially weaker crystal peaks or no peaks at all. XRD ($\theta - 2\theta$) scans displayed strong (002) peaks for both nitride films grown on sapphire substrates, confirming the monocrystalline epitaxial character of the synthesized GaN/sapphire and InN/sapphire samples. The impact of plasma gas mixture and Ar-plasma annealing process revealed different results for GaN versus InN films. While H_2-containing plasmas are optimal for GaN, InN prefers H_2-free plasma gas mixtures. Also, Ar-plasma annealing improved GaN film properties while degrading InN film quality.

3:00pm EM-WeA-7 Epitaxial Rare-Earth Orthoferrites by Atomic Layer Deposition, *Linn Rykkje, H. Sønsteby, O. Nilsen,* University of Oslo, Norway

Rare earth orthoferrites ($RFeO_3$, R = lanthanide) are a class of materials whose optical and multiferroic properties demonstrate a rich landscape of functionalities. While their ferroelectric and -magnetic behavior are interesting in themselves, it is the potential for magnetoelectrically coupled behavior that make them fascinating candidates for applications in photoferroics [1][2], photocathodes [3]**,** spintronics [4][5], gas sensing [6], and memory storage [1], among others.

The number of studies on orthoferrites has seen a rise in tandem with a growing awareness of their potential, but much of their fundamental behavior remains to be elucidated. Compared to more renowned multiferroics, like $BiFeO_3$, the rare earth orthoferrites are practically unexplored, despite exhibiting very similar characteristics.

A particularly interesting member to study is $NdFeO_3$, which, based on first principles calculations, is located near a multiphase boundary and could exhibit a giant polarization in a phase reminiscent of $BiFeO_3$[7][8].

To achieve such giant polarization, it would be necessary to impose significant compressive strain or apply chemical pressure (through the choice of rare earth) - both of which are highly compatible with the control leveraged by ALD as shown in our previous work. A second pathway towards functionalization is via A- or B-site substitution – which is also attainable by ALD.

The work presented here demonstrates a viable ALD synthesis route for $NdFeO_3$ thin films with tunable chemical composition and crystallinity

achieved after annealing. The growth of the binary oxide layers (Nd_2O_3 and Fe_2O_3) on surfaces terminated by each other has been thoroughly investigated using quart crystal microbalance (QCM) and found to differ significantly. This is surprising given the similarity of the cation precursors used.

While the thin films have not been electrically conductive or any polarization tested at the time of writing, we believe that our approach will shed light on the structure-property relations of an elusive group of materials that are candidates for new functionality in a range of applications. We present characteristics of the ALD-process(es), as well as initial results on structural integrity and functionality.

For references, see Supplemental Document.

3:15pm **EM-WeA-8 Area Selectivity and Crystallographic Orientation of ZIF-8 Films Deposited by Molecular Layer Deposition**, *Jorid Smets*, *V. Rubio-Giménez,* KU Leuven, Belgium*; S. Armini,* IMEC Belgium*; R. Ameloot,* KU Leuven, Belgium

Integrating metal-organic frameworks (MOFs) into microfabrication processing requires highly controlled vapor-phase deposition techniques. This study presents a vapor-phase method that enables crystallographic control and direct area-selective deposition of zeolitic imidazolate framework 8 (ZIF-8). The deposition process involves a two-step ZIF-8 molecular layer deposition (MLD), during which an amorphous precursor layer is initially deposited through consecutive self-saturating reactions of diethyl zinc, water, and 2-methylimidazole. Subsequently, a linker post-treatment step promotes crystallization. The use of substrates functionalized with self-assembled monolayers (SAMs) with different head moieties allows tuning the degree of crystalline orientation in the resulting MOF layers. Additionally, the functional groups of the SAMs influence the mobility of the ZIF-8 building blocks on the surface, enabling control over the surface coverage through area-dependent surface diffusion. By exploiting this phenomenon, we successfully achieved direct area-selective deposition of ZIF-8, which can facilitate the integration of MOFs into microelectronics.

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