Tuesday Evening, August 6, 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.

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EM-TuP-5 Low Temperature Plasma Synthesis of Layer controlled MoS_2 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.

This work was supported by the Technology Innovation Program (Public-private joint investment semiconductor R&D program(K-CHIPS) to foster high-quality human resources)(RS-2023-00235484, "Development of High Quality MX2 Materials and Processes through In-situ Defect Analysis") funded By the Ministry of Trade, Industry & Energy(MOTIE, Korea)(1415187770)

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.

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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 TiO_2 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

TiO_2 has been intensively studied as a transparent conductive oxide and photoanode for photovoltaic and photocatalytic applications. The conductivity of TiO_2 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 TiO_2 by thermal ALD and the effect of doping and annealing conditions on the structural and electrical properties of Ta: TiO_2 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 TiO_2 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.

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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.

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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 buffler 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.

[1] Y. Ren, E.K. McGuinness, et al., Chem. of Mat. 33 (2021)

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).

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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$_2$O$_4$ 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.

1: Pinna, N; Knez, M.; *Atomic Layer Deposition of Nanostructured Materials*; Wiley-VCH, 2011, p. 99-102

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$_2$O$_3$ 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.

1. S.J. Zheng, I.J. Beyerlein, J. Wang, J.S. Carpenter, W.Z. Han, N.A. Mara, Acta Materialia, 60 (2012) 5858-5866.

2. N. Mara, I. Beyerlein, J Mater Sci, 49 (2014) 6497-6516.

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