Wednesday Morning, June 30, 2021

Live Session

Room Live - Session LI-ALD-WeM2

AM/AF (in-situ metro) Live Session

Moderators: Dr. Alex Martinson, Argonne National Laboratory, Dr. Nathanaelle Schneider, CNRS-IPVF, Dr. Virginia Wheeler, U.S. Naval Research Laboratory

9:30am **LI-ALD-WeM2-1 Welcome, Thank Yous & Instructions**, *Nathanelle Schneider*, CNRS-IPVF, France

Thank you for attending today's session! We hope you will enjoy the session!

9:35am **LI-ALD-WeM2-2 Surface Modification of TiO₂ Nanoparticles by Ultrathin SiO₂ Films, Cu₂O and Pt Nanoclusters for Enhanced Photocatalytic Activity Using Atomic Layer Deposition in a Fluidized Bed Reactor: A Comparative Study**, *Hao Van Bui,* Phenikaa University, Viet Nam*; D. Benz, J. van Ommen,* Delft University of Technology, Netherlands **INVITED**

Titanium dioxide (TiO_2) is the most popularly used photocatalyst in many practical applications, such as air purification, water treatment, and hydrogen production due to its excellent photocatalytic properties, high structural and chemical stabilities, low environmental impact, and abundance in nature. However, the rapid recombination of photogenerated electrons and holes is a major limiting factor to achieve high photocatalytic efficiencies. To address this issue, the surface of TiO_2 is usually engineered by coupling with a thin film or nanoclusters of other materials. This is to promote the charge transfer at the interface between the TiO_2 and the deposited materials, which consequently reduces the charge recombination in the TiO_2.

Due to their high catalytic activities, noble metals are most popularly used. In addition to promoting electron transfer, noble metals can also act as co-catalysts, providing further catalytic enhancement. Nevertheless, long exposures to UV-irradiation may cause local photocatalytic oxidation of the metal at the metal/TiO_2 interfaces, which creates new electron-hole recombination centers and consequently decreases the photocatalytic efficiency. In addition, despite their excellent activity, the use of noble metals is not desirable due to their high cost and scarcity, especially for large-scale production. Therefore, the surface modification of TiO_2 by oxides such as CuO, Cu_2O, Fe_2O_3, and SiO_2 has recently been more attractive.

Our presentation will focus on the use of ALD in a fluidized bed reactor operating at atmospheric pressure (APALD-FBR) for the surface modification of TiO_2 nanoparticles. Three different ALD processes are demonstrated: ALD of ultrathin SiO_2 films using $TiCl_4$ and H_2O, ALD of Cu_2O using $Cu(I)(hfac)(TMVS)$ and H_2O, and ALD of Pt using $MeCpPtMe_3$ and O_2. We will show that APALD-FBR not only provides the ability to control the deposition of SiO_2, Cu_2O, and Pt at the sub-nanometer scale but also enables the deposition at temperatures significantly lower than the conventional ALD processes. We will further demonstrate that the photocatalytic activity of TiO_2 depends strongly on the loading of the deposited material (SiO_2, Cu_2O, or Pt) and by controlling the loading, the photocatalytic activity of TiO_2 can be significantly enhanced. A comparison of the photocatalytic activities of TiO_2/SiO_2, TiO_2/Cu_2O, and TiO_2/Pt photocatalysts toward the degradation of various organic dyes will be presented and discussed.

9:55am **LI-ALD-WeM2-6 In-Situ High Temperature XRD of Atomic Layer Deposited Gallia-Ceria Mixed Oxides**, *Fatemeh Gashoul Daresibi,* University of Tehran, Iran*; M. Heikkilä, M. Ritala,* University of Helsinki, Finland*; A. Khodadadi, Y. Mortazavi,* University of Tehran, Iran

Ceria is well-known for its oxygen storage-release capacity [1]. Catalytic behavior of ceria can be tuned by mixing it with different oxides including those of V [2], Ga [3] and Zr [4]. Although the control on the stoichiometry and close contact of oxides is highly challenging [5], recent studies on atomic layer deposition [6] showed its capability in synthesizing conformal and uniform film with atomically precise control of composition.

Herein, we synthesized $Ga_xCe_yO_z$ with super-cyclic ALD using $Ce(thd)_4$, $Ga(acac)_3$ and O_3. Studies on the growth rate showed surface enhanced and linear growth at low and high number of cycles respectively. The in-situ HT-XRD of pure ceria showed changes of crystal structure at high temperatures starting from 650°C under H_2 and a constant lattice structure under air. The XRD pattern of $Ga_xCe_yO_z$ in oxidizing atmosphere under air did not show any specific peak from RT up to 600°C due to incorporation of Ga in cerium oxide and then characteristic peaks of crystalline ceria appeared at higher

temperatures as a sign of segregation and phase separation [7]. In reducing atmosphere, under H_2, the evolution of a weak crystalline structure was monitored which peered to be related to the ceria when the partially reduced gallium oxide started to evaporate and leave the mixed oxide film [8]. The results showed that this surface segregation only happens at temperatures high enough to locally reduce and sublime the gallium species. Ex-situ Raman spectra and atomic force microscopy of the samples calcined at various temperatures also confirmed the crystallization/roughening of the films at high calcination temperatures. Therefore, the ALD-GaCeOₓ thin film keeps its amorphous mixed structure stable up to around 600°C suitable for many catalytic reactions.

References:

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10:10am **LI-ALD-WeM2-9 Using Ambient Pressure X-Ray Photoelectron Spectroscopy to Study ALD in real-time**, *Esko Kokkonen,* Max IV Laboratory, Sweden*; M. Kaipio, H. Nieminen,* University of Helsinki, Finland*; F. Rehman,* Lund University, Sweden*; V. Miikkulainen,* Aalto University, Finland*; M. Putkonen, M. Ritala, S. Huotari,* University of Helsinki, Finland*; J. Schnadt,* Lund University, Sweden*; S. Urpelainen,* University of Oulu, Finland

Ambient pressure X-ray photoelectron spectroscopy (APXPS) is a powerful tool to study surfaces in elevated pressure and temperature conditions. We have recently developed an ambient pressure cell (AP cell) dedicated to ALD research. The cell allows studying the surface of a substrate where ALD reactions take place. Importantly, since the cell makes it possible to conduct XPS measurements at millibar pressure regimes, it is possible to measure the chemical state of the surface in real-time as the ALD precursors react with the surface. The cell is intended for chemical characterization of intermediate products that are short-lived and might not be present on the surface once saturation of the surface has been achieved and therefore are not visible in post-process XPS identification. Experiments such as these have gained noticeable traction within a few years. [1,2]

The system is installed on the SPECIES beamline [3] at the MAX IV Laboratory in Lund, Sweden. SPECIES is a soft X-ray beamline with one beam branch dedicated to APXPS. The beamline offers a wide photon energy range of 30-1500 eV, which enables to study most core-levels using XPS, but also makes it possible to focus on valence band investigations using UPS and lower photon energies and high photon flux. The endstation consists of different equipment for sample characterization and preparation, with the main instrument being an electron analyser capable of high energy and time resolution.

The ALD cell has been designed with realistic gas flow dynamics in mind. The cell can be operated with a maximum pressure of 20 mbar, with the intention of creating a laminar-like flow across the substrate surface that is being investigated using XPS. The outlet (pump) line of the cell is connected to a quadrupole mass spectrometer (QMS) via a leak valve. The QMS allows to simultaneously follow masses of important ligands and synchronize this data acquisition with the XPS data.

Here, we will give a brief overview of the system including its design and operating parameters. Some results from example cases are given which demonstrate the capability of the ALD cell for studying substrates during ALD reactions.

References:

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[2] R. Timm, et al. "Self-cleaning and surface chemical reactions during hafnium dioxide atomic layer deposition on indium arsenide." *Nature communications* **9**, 1, 1-9 **(2018)**

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10:25am LI-ALD-WeM2-12 Observing the Crystallization of Ultrathin Alumina and Polymorphic Transformations of Gallium Oxide Using *in Situ* Reflection High Energy Electron Diffraction*, Alexandra Howzen, N. Strandwitz,* Lehigh University

The maximum amount of thermal energy available during atomic layer deposition (ALD) is generally determined by the decomposition temperature of the precursors which also sets the maximum temperature for the "ALD window". This maximum temperature limits the structural perfection and extent of crystallization in resulting films for many ALD precursor chemistries. Intermittent annealing during the film growth in between ALD chemical exposures has been explored previously and is shown to increase the density and quality of ALD films[1]. However, the ability to directly monitor structural changes of ALD films is expected to provide new insight regarding film crystallization temperature, surface roughening, and dependence on gas ambient.

In this work, we integrate reflection high energy electron diffraction (RHEED) into a home-built ALD system to monitor structural and morphological transformations during ALD growth and thermally-induced structural transformations. RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. We will use *in situ* RHEED to observe the thermal crystallization of an ultrathin, amorphous alumina film deposited on sapphire. Similarly, we will show the thermally induced structural evolution of an ultrathin (1-20 ALD cycles) Ga_2O_3 film deposited on sapphire with $TMGa/O_2$ precursors. Ga_2O_3 films display multiple polymorphs (α, β, γ, δ, ε) which can be controlled depending on substrate crystal structure and crystallization temperature. Therefore, this work shows the structural transformations available to ultrathin Ga_2O_3 films deposited by ALD as a function of temperature up to the film's complete desorption. The integration of RHEED with ALD offers a slow-motion picture of the structural transformations that occur during traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

1 J.F. Conley, Y. Ono, and D.J. Tweet, Appl. Phys. Lett. 84, 1913 (2004).

10:50am LI-ALD-WeM2-17 Novel Functional Metal-Organic Materials by ALD/MLD*, Maarit Karppinen,* Aalto University, Finland   INVITED

Atomic layer deposition (ALD) technology is one of the cornerstones of modern microelectronics, where it is exploited in the fabrication of high-quality conformal inorganic thin films. Its counterpart for organic thin films – molecular layer deposition (MLD) – has also been known for long but little exploited. Currently, the hybrid of these techniques – ALD/MLD – is strongly emerging as a state-of-the-art route for designer's metal-organic thin films. In ALD/MLD, a metal-bearing precursor is combined with an organic precursor to deposit metal-organic thin films in which the organic molecules naturally link the metal atoms. Interestingly, some of these processes yield in-situ crystalline films. Another intriguing aspect is that many of the metal-organic materials realized through ALD/MLD are fundamentally new and difficult if not impossible to be obtained through conventional synthesis. In this presentation my intension is to [1-7]: (*i*) briefly introduce the breath of the ALD/MLD processes developed, (*ii*) address the constraints/possibilities for growing in-situ crystalline metal-organic thin films, and (*iii*) highlight some exciting ALD/MLD materials and their application potential e.g. in microbatteries, solar cells and flexible magnets.

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2. J. Heiska, M. Nisula & M. Karppinen, Organic electrode materials with solid-state battery technology, *J. Mater. Chem. A***7**, 18735 (2019).
3. J. Multia, J. Heiska, A. Khayyami & M. Karppinen, Electrochemically active in-situ crystalline lithium-organic thin films by ALD/MLD, *ACS Appl. Mater. Interfaces***12**, 41557 (2020).
4. J. Heiska, M. Madadi & M. Karppinen, CO_2-based atomic/molecular layer deposition of lithium ethylene carbonate thin films, *Nanoscale Adv.***2**, 2441 (2020).
5. Z. Giedraityte, M. Tuomisto, M. Lastusaari & M. Karppinen, Three- and two-photon NIR-to-vis (Yb,Er) upconversion from ALD/MLD fabricated molecular hybrid thin films, *ACS Appl. Mater. Interfaces***10**, 8845 (2018).
6. A. Ghazy, M. Safdar, M. Lastusaari, A. Aho, A. Tukiainen, H. Savin, M. Guina & M. Karppinen, Luminescent(Er,Ho)$_2$O$_3$ thin films by ALD to enhance the performance of silicon solarcells, *Sol. Ener. Mater. Sol. Cells***219**, 110787 (2021).
7. A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe$_2$O$_3$-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces***12**, 21912 (2020).

11:10am LI-ALD-WeM2-21 Ultrathin Hybrid Siloxane-Alumina Dielectric Films by Ring Opening Molecular Layer Deposition of Cyclic Tetrasiloxane*, Kristina Ashurbekova,* Dagestan State University , Russian Federation*; K. Ashurbekova,* CIC nanoGUNE BRTA, Spain*; I. Saric,* University of Rijeka , Croatia*; M. Gobbi, E. Modin, A. Chuvilin,* CIC nanoGUNE BRTA, Spain*; M. Petravic,* University of Rijeka, Croatia*; I. Abdulagatov,* Dagestan State University, Russian Federation*; M. Knez,* CIC nanoGUNE BRTA, Spain

Siloxane-based materials have gained interest for various important applications such as insulating layers in microelectronics, thin film encapsulation layers, biocompatible coatings, and barriers. The ring-opening polymerization (ROP) of cyclic siloxanes is a way to synthesize such materials using solution-based techniques and is a rare example of an entropically driven polymerization. The vibrational and rotational freedom achievable in the linear siloxane units is much greater than in the cyclic structures. In this work, we introduce cyclic siloxanes as a new class of silicon precursors for ROP- Molecular layer deposition (MLD), uncommon because of the lack of reactive groups, but reactive because of the ring structure of the cyclosiloxane.

MLD is a powerful vapor phase approach for growing thin polymer films with molecular level thickness control. In the present work, hybrid organic-inorganic siloxane-alumina films were grown by applying a ring-opening MLD using sequential surface reactions between 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4D_4) and trimethylaluminum (TMA). *In-situ* QCM analysis showed a linear mass increase with the number of MLD cycles within a processing temperature window between 120 and 200 °C and revealed a self-limiting surface chemistry between TMA and V_4D_4. A growth per cycle of 1.4 and 1.6 Å and a density of 1.9 and 2.2 g/cm^3 were determined by X-ray reflectivity (XRR) for the V_4D_4/TMA film deposited at 150 and 200 °C, respectively. X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and in-situ QCM were employed to analyze the structural changes, composition of the film and to suggest a realistic V_4D_4/TMA reaction mechanism. High-resolution transmission electron microscopy (HRTEM) showed that the MLD process enables the formation of highly conformal coating of zirconia nanoparticles. The grown siloxane-alumina film, even as thin as 12 nm, showed an extremely low leakage current density (lower than 5.1×10^{-8} A cm^{-2} at ± 2.5 MV cm^{-1}), a dielectric constant (k) of 4.7, and a good thermal stability after one-hour annealing in air at 1100 °C. The pinhole-free nature and conformal growth inherent to the MLD technique allow the formation of high-quality siloxane-alumina thin films withexcellent insulating properties and thermal stability that are promising as ultrathin insulating coatings in field-effect transistors, flash memories, and capacitors in modern electronic systems. [1]

[1] Ashurbekova Kr., et al. *Chemistry of Materials.* 2021. DOI: 10.1021/acs.chemmater.0c04408

11:25am LI-ALD-WeM2-24 Optically Controlled Large-Coercivity Room-Temperature Thin-Film Magnets Through ALD/MLD*, Anish Philip, M. Karppinen,* Aalto University, Finland

Optically controlled magnetic materials could enable magnetic ultra-fast recording at high density. Such dream materials designed from multiple functionalities could open new horizons for many other application fields as well requiring photo-controlled nanoswitchers.[1] Though there are several families of photomagnetic materials known, including the prussian blue analogues,magnetic nanoparticles modified with photochromic molecules and inorganic materials intercalated with photoresponsive molecules, the real challenges of discovering photo-magnets performing at room-temperature and fabricated in thin films using an industrially feasible technology have never been addressed.

Here we address the challenge by taking the advantage of the atomic/molecular layer deposition (ALD/MLD) technique.[2–4]We deposited ε-Fe$_2$O$_3$:azobenzoate superlattice structures with sub-nm scale accuracy from FeCl$_3$, H$_2$O and azobenzene-4,4'-dicarboxylic acid precursors. The ε-Fe$_2$O$_3$ phase was chosen due to its unique room-temperature multiferroic properties including an exceptionally high coercive field.Azobenzene is a

well-known photochromic molecule and has been used for integrating into several functional materials as it undergoes reversible isomerization (trans-cis) around the N=N bond upon light irradiation of suitable wavelengths.By combining the RT hard ferrimagnet ε-Fe₂O₃ and the photoresponsive azobenzene,we demonstrate the reversible photo-switching functionality on the coercivity and magnetization values with alternating irradiations of the films with UV and visible light. Interestingly, the azobenzene layers not only add the switching functionality but also enhance the overall magnetic performance of the ε-Fe₂O₃ matrix. For example, the room-temperature coercivity was found to be 2.6 kOe for ε-Fe₂O₃-azobenzoate superlattice structures, while it was 2.0 kOe for a ε-Fe₂O₃ film of the same overall thickness.

A vibrating sample magnetometer (VSM) was used for studying the magnetic properties of the films. The structure, chemical composition and photoresponsive nature of the films were investigated using XRR, GIXRD, SEM, FTIR and UV-Vis studies.

References

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11:40am LI-ALD-WeM2-27 Deposition of Thermally Stable Polybenzimidazole (PBI) Thin Films by Molecular Layer Deposition Technique, *Saba Ghafourisaleh*, *M. Leskelä, M. Putkonen, M. Ritala,* University of Helsinki, Finland

We report the deposition of polybenzimidazoles (PBI) thin films with Molecular Layer Deposition (MLD) for the first time. Imidazole derivatives are known to be thermally stable and withstand harsh acidic, basic, and oxidizing environments. MLD process for PBI-like polymers would open up numerous application fields where conformal organic thin films can be used as protective layers for more sensitive materials, like thermally resistant textile fibers, thermal insulation parts of semiconductor devices, high-temperature matrix resins, adhesives, and foams. Previously inorganic ALD materials, like Al₂O₃, have been used for protecting polymers.[1,2]

Isophthalic acid (IPA), 3, 3'-diaminobenzidine (DAB) were used as monomers and TMA was used as a promoting precursor in this process. The monomers were pulsed and purged sequentially and the condensation reactions of the adsorbed monomers on the surface resulted in PBI thin film growth with growth are of 6.0 Å/cycle. PBI films were characterized in detail by FTIR, SEM, TGA/DTA, and AFM.

Sublimation temperatures for the IPA and DAB were 160-165 °C and 210-220 °C, respectively. The reaction temperature was within a range of 225-300 °C. The films were uniform and transparent on a silicon substrate. The thickness non-uniformity along the 5x5 cm² substrate was less than 2 %. The films were smooth with a low degree of roughness (500 nm x 500 nm, Rq=0,48 nm for 1µm thick film). Thermogravimetry (TGA) analysis in nitrogen (N₂) and air showed that PBI films were thermally stable.

References

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11:55am LI-ALD-WeM2-30 Future of Membrane Separations through Atomic Layer Processing, *David Bergsman,* University of Washington **INVITED**

Recent years have seen a surge of interest into improving the scalability of atomic layer processing (ALP) tools, such as work in spatial atomic layer deposition (ALD), molecular layer deposition (MLD), and vapor-phase infiltration (VPI). This improved scalability, along with a continued decrease in the cost of these processes, has allowed these tools to be considered outside the semiconductor industry, such as in solar cells and battery electrodes. These are technologies for which precise control over thickness, structure, and composition is critical to achieve optimum device performance. One technology area that has yet to see commercialization of these tools is in membrane separations. Similar to solar cells and batteries, membranes also rely upon precise materials properties to operate effectively, requiring narrow pore size distributions, non-fouling surface chemistries, and robust rheological properties. As a result, membranes are an excellent candidate for the implementation of atomic layer processing tools in their synthesis.

This presentation will highlight the potential use of atomic layer processing tools for membrane separations, reviewing recent advancements in this area. Generally, these tools can either be used to enhance an already existing material, such as by coating a porous structure or infiltrating a bulk material, or they can be used to create the selective layer itself, through the deposition of a thin selective layer. First, the use of ALD, MLD, and VPI to enhance membrane performance will be highlighted, including work to decorate membrane surfaces, control pore sizes, and infiltrate polymers to impart conductivity or chemical resilience. Then, cases where ALD and MLD have been used to create the active separating layer will be discussed, such as in ALD-based inorganic ion conductors, MLD-based desalination membranes, and hybrid ALD/MLD-based porous layers. Finally, promising future directions and the improvements that will ultimately be necessary for these tools to be used in commercial membrane synthesis will be explored.

12:30pm LI-ALD-WeM2-37 Molecular Layer Deposition of All-Organic Polyamide Nylon 6,2, *Marcel Junige, S. George,* University of Colorado at Boulder

We developed an MLD process for the all-organic polyamide nylon 6,2 using separate, sequential exposures of ethylene diamine and adipoyl chloride. Our hot-wall, viscous-flow vacuum reactor featured a small gas volume, laminar gas flow conditions, and isothermal heating. We utilized *in situ* spectroscopic ellipsometry (iSE) to study MLD nucleation and growth; as well as x-ray reflectometry (XRR), atomic force microscopy (AFM), x-ray photoelectron spectroscopy, Raman spectroscopy, and grazing-incidence small- & wide-angle x-ray scattering to characterize MLD film properties.

In the steady-state growth regime, iSE verified the MLD characteristics: Multiple exposures of neither monomer alone could produce a significant thickness gain; both the half-reactions were self-terminating. The MLD exhibited a linear growth per cycle (GPC) of 3.7 Å at 115ºC. The GPC decreased by approximately 1/3 with every 10ºC increase in temperature.

The refractive index of a ~100 nm nylon 6,2 MLD film was extracted from an iSE multi-time-slice analysis and exhibited uniaxial anisotropy. This anisotropy indicated an orderly alignment of individual polymer chains. Amine hydrogen from one polyamide chain can bridge bond with carbonyl oxygen from another. These intermolecular forces can hold nylon chains together very tightly. XRR measured a mass density of 1.38 $^g/_{cm^3}$, matching the calculated crystal density value. AFM imaged the surface of a ~17 nm nylon 6,2 MLD film: The rms roughness of 4.4 Å was characterized from the topography image; the Young's modulus, averaging 3.6±0.5 GPa, was extracted from force-distance curves in pinpoint mode at every pixel. This verified uniform nanomechanical film properties without pinholes.

We also tested the stability of nylon 6,2 MLD films in various atmospheres at temperatures from 115 to 350ºC. Nylon 6,2 MLD films started to lose thickness in argon around 150ºC. Neither acetone vapor nor molecular oxygen etched nylon 6,2 at 135°C. In contrast, hydrogen peroxide vapor and ozone spontaneously etched nylon 6,2.

In related work, we have demonstrated area selectivity of nylon 6,2 MLD on industrial test features with nucleation and growth on amorphous carbon lines versus inhibition on passivated silica trenches.[1] We utilized secondary electron microscopy to image the test features before and after area-selective MLD. This demonstrated the potential to repair the amorphous carbon hard mask that eroded by reactive ion etching during pattern transfer. The all-organic polymer nylon 6,2 was preferable because no residue was left after ashing of the MLD films.

1. *JVST A* **39**, 023204 (2021).

Wednesday Morning, June 30, 2021

12:45pm LI-ALD-WeM2-40 Vapor Phase Conversion of Pt Nanoparticles Into Pt-Sn Bimetallic Nanoparticles, *Nithin Poonkottil*, R. Ramachandran, Ghent University, Belgium; *E. Solano*, ALBA Synchrotron, Spain; *N. Veeraraghavan Srinath, J. Feng, A. Werbrouck, M. Van Daele, M. M. Minjauw, M. Filez, H. Poelman*, Ghent University, Belgium; *A. Coati*, Synchrotron SOLEIL, France; *C. Detavernier, J. Dendooven*, Ghent University, Belgium

Bimetallic nanoparticles (BMNPs) offer interesting size and composition-dependent properties. Pt-Sn BMNPs are important in the field of catalysis, highlighted by their widespread industrial use for propylene production. They are widely accepted as a model system in fundamental studies of structure-performance relationships. ALD has proven successful in preparing catalytic systems with fine control over NP sizes and compositions, but the creation of non-noble metal-containing alloys often requires a high temperature reduction step. We report the vapour phase conversion of Pt NPs into Pt-Sn BMNPs based on the selective decomposition of tetrakis(dimethylamido)tin (TDMASn), a common Sn ALD precursor, on Pt, which induces a solid-state reaction of metallic Sn with Pt to form BMNPs at low temperature.

The decomposition of ALD precursors is often mainly considered a temperature dependent property. However, TDMASn provides an example where the precursor decomposition is also a substrate dependent property. We found that TDMASn selectively decomposes on Pt in a temperature range of 150-300°C, whereas no decomposition was observed on other substrates like SiO_2, Al_2O_3 and TiN (Fig.1a). The decomposition of TDMASn on Pt thin films led to the formation of different Pt-Sn alloys (Fig.1b). The exposure of ALD-grown Pt NPs (Fig.2a) to TDMASn pulses resulted in their conversion to Pt-Sn BMNPs, but the conversion process induced extensive particle ripening, leading to large and non-uniform particle sizes, undesired for catalytic applications (Fig.2c). Interestingly, the conversion process could be improved by using an alternating pulsing sequence of TDMASn and H_2 exposures. The introduction of H_2 substantially aids in retaining the small NP sizes of the original Pt NPs (Fig.2b). In situ mass spectrometry data during this process showed the removal of organic ligands during the H_2 pulse. The Sn uptake was monitored by in situ X-ray fluorescence (XRF), revealing saturation of the Sn incorporation in the Pt NPs as a function of the number of TDMASn-H_2 conversion cycles (Fig.3a). Moreover, the amount of inserted Sn can be controlled via the deposition temperature. PtSn versus Pt_3Sn is accomplished by varying the deposition temperature during this process from 150-250°C (Fig.3b). Finally, we confirmed the compatibility of this method with high surface area supports by the successful conversion of a mesoporous Pt/SiO_2 catalyst.

1. Ramachandran et al., RSC advances 2017, 7 (33), 20201-20205.

1:00pm LI-ALD-WeM2-43 Atomic Layer Deposition of Zirconium Sulfide, *Xiangbo Meng*, University of Arkansas

Zirconium disulfide (ZrS_2) is one of two-dimensional (2D) transition metal dichalcogenides (TMDs), which is promising in many applications, such as lubrication, optoelectronic, catalysis, and energy storage. However, few studies have been devoted to developing ZrS_2. As a unique technique, atomic layer deposition (ALD) has been reported for a variety of sulfide processes in the past decades and recently emerged as a new tool for nanofabrication of 2D TMDs.[1,2] Using tetrakis(dimethylamido)zirconium(TDMA-Zr) and 4% H_2S as precursors, recently we have developed a novel ALD process to grow ZrS_x. Similar precursors have been used in our previous studies.[3-5] We first investigated the ALD ZrS_x process using an *in situ* quartz crystal microbalance (QCM) and our QCM measurements confirmed repeatable saturation growth of ZrS_x at different temperatures. Our study further revealed that this ALD process enables large-scale growth of nanoscale ZrS_x films uniformly in the temperature range of 75 – 300 ℃ on various substrates. Furthermore, we characterized the ALD ZrS_x films using a suite of tools, including scanning electron microscopy, transmission electron microscopy, synchrotron-based X-ray diffraction, and X-ray photoelectron spectroscopy to clarify their morphology, crystallinity, and composition. We found that the growth of ZrS_x per cycle decreases from 1.17 Å/cycle at 75 ℃ to 0.28 Å/cycle at 300 ℃. In addition, our work revealed that the crystallinity and composition of ZrS_x compounds vary with deposition temperature. This study may pave an avenue to grow large-scale 2D ZrS_2 films, which potentially provide new solutions to some emerging applications.

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5. *Chem. Mater.*, 2014, **26**, 1029-1039.

1:15pm LI-ALD-WeM2-46 Vapor Phase Infiltration of Titanium Tetrachloride Into Polyaniline (PANI): Process Kinetics, Electronic Properties and Optical Response, *Mark Losego*, S. Gregory, Y. Li, K. Malinowski, Georgia Tech

This talk with discuss our use of vapor phase infiltration (VPI) to alter the optoelectronic properties of conducting polymer poly(aniline) (PAni). VPI is similar to atomic layer deposition (ALD), but instead of cycling viscous flows of co-reactants, VPI doses a single reactant vapor in a static atmosphere followed by a pump-purge cycle. ALD typically provides conformal surface coatings while VPI enables extensive sub-surface diffusion and reactions within organic substrates. In particular to our study, PAni was VPI treated with a single cycle of $TiCl_4$-H_2O, and the resulting hybrid films showed unique optoelectronic properties that have not been previously reported. As VPI hold time increased, PAni films turned from blue to nearly transparent to green. This color transition is because of the formation of polaronic charge carriers concomitant with the formation of TiO_x; the polaronic carriers absorb the red-NIR-MIR spectra (700- 5000 nm) while TiO_{-x} absorb the blue-UV region (450 - 350 nm). This combination of optical absorbances in PAni has not been observed before. Furthermore, these polaronic carriers enabled electrical conductivities as high at 0.2 S/cm. By varying the $TiCl_4$ exposure time and measuring *ex-situ-* optical signatures, an effective diffusion coefficient of *ca.* $1 \cdot 10^{-15}$ cm^2/s was measured. Lastly, XPS measurements elucidated a reaction mechanism for the formation of TiO_{-x} and PAni polarons. Both oxidative doping and acid doping due to the HCl byproduct is observed. By better understanding this reaction mechanism and kinetics, ALD and VPI can be optimized for future organic semiconductor doping processes.

1:30pm LI-ALD-WeM2-49 Atomic/Molecular Layer Deposition for Batteries Materials, *Chunmei Ban*, University of Colorado Boulder **INVITED**

The atomic layer deposition (ALD) technique has proven itself to be the best method to deposit continuous, conformal and pinhole-free films. Ultrathin metal oxides coating via ALD has been applied on battery materials in mitigating the parasitic side reactions between the electrolyte and the electrode surface, which results in the greatly improved performance of lithium-ion electrodes. Based on the similar deposition mechanism, we have developed molecular layer deposition (MLD) to integrate organic groups into the metal oxides matrix, in order to simultaneously address both mechanical strength and surface stability. It is found that the inherent non-passivating behavior of electrode materials in the organic lithium-ion battery electrolyte results in large irreversible capacity loss and gradual electrolyte consumption during operation. Such interaction between electrolyte and electrode becomes more pronounced for intermetallic alloy and lithium-metal anode materials and high-voltage cathode materials. This presentation will discuss the mitigation strategies which are based on atomic/molecular deposition techniques and their impact on electrochemical behavior of battery materials. With the capability to modify the surface and interface through the control of composition, thickness and mechanical properties, MLD would chemically or physically change the surface chemistry and structure of battery materials, while accommodating dramatic volumetric change associated with high-capacity intermetallic anodes. Combining with the results from advanced characterization techniques, this talk will emphasize the unique chemical interaction between the electrolyte and the surface of intermetallic electrodes, and exploit surface modification strategies to dictate the interface chemistry and manipulating the chemi-physical properties of the electrode-electrolyte interphase for efficient electrochemical reactions.

1:50pm LI-ALD-WeM2-53 Announcement of ALD and ALE Student Awardees, Closing Remarks & Thank Yous, *Seán Barry*, Carleton University, Canada

Thank you for attending the ALD/ALE 2021 Virtual Meeting! We will see you at ALD/ALE 2022, June 26-29, 2022, Ghent, Belgium.

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