Emerging Materials
Room Plaza E - Session EM+AA-MoA

Organic-Inorganic Hybrid Materials & MLD (1:30-3:30 pm)/Catalysis and Fuel Cells II (4:00-5:30 pm)

Moderators: Sang In Lee, Synos Foundation, Yongfeng Mei, Fudan University, China, Ville Miikkulainen, University of Helsinki

1:30pm **EM+AA-MoA-1 Unique Inorganic-Organic Hybrid Materials by ALD/MLD as Enablers of Next-generation Applications?**, ***Maarit Karppinen,*** Aalto University, Finland **INVITED**

The combined ALD/MLD approach has the capacity to yield unique functional hybrid materials, consisting of finely-tuned combinations of inorganic and organic components and possessing a property palette that may reach properties even beyond those directly derived from the component inorganics and organics. These materials are formed through different bonding schemes and may be amorphous or crystalline, isotropic or organized into different superlattice structures. Our recent works[1-9] have demonstrated e.g. exciting coordination-network or MOF-type crystal structures, attractive heat and Li-ion conduction properties, and various luminescence phenomena, relevant to next-generation applications in e.g. flexible heat harvesters, photoconverters, microbatteries, sensors or catalysts.

1. T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, Efficiently suppressed thermal conductivity in ZnO thin films via periodic introduction of organic layers, *J. Mater. Chem. A* **2**, 12150 (2014).

2. J.-P. Niemelä, A, Giri, P.E. Hopkins & M. Karppinen, Ultra-low thermal conductivity in TiO_2:C superlattices, *J. Mater. Chem. A* **3**, 11527 (2015).

3. Z. Giedraityte, P. Sundberg & M. Karppinen, Flexible inorganic-organic thin-film phosphors by ALD/MLD, *J. Mater. Chem. C* **3**, 12316 (2015).

4. Z. Giedraityte, L.-S. Johansson & M. Karppinen, ALD/MLD fabrication of luminescent Eu-organic hybrid thin films using different aromatic carboxylic acid components with N and O donors, *RSC Adv.* **6**, 103412 (2016).

5. Z. Giedraityte, O. Lopez-Acevedo, L.A. Espinosa Leal, V. Pale, J. Sainio, T.S. Tripathi & M. Karppinen, Three-dimensional uracil network with sodium as a linker, *J. Phys. Chem. C* **120**, 26342 (2016).

6. E. Ahvenniemi & M. Karppinen, Atomic/molecular layer deposition: a direct gas-phase route to crystalline metal-organic framework thin films, *Chem. Commun.* **52**, 1139 (2016).

7. E. Ahvenniemi & M. Karppinen, In-situ atomic/molecular layer-by-layer deposition of inorganic-organic coordination network thin films from gaseous precursors, *Chem. Mater.* **28**, 6260 (2016).

8. M. Nisula & M. Karppinen, Atomic/molecular layer deposition of lithium terephthalate thin films as high rate capability Li-ion battery anodes, *Nano Lett.* **16**, 1276 (2016).

9. M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, Lithium aryloxide thin films with guest-induced structural transformation by ALD/MLD, *Chem. Eur. J.*, in press (2017).

2:00pm **EM+AA-MoA-3 Atomic/molecular Layer Deposition of Luminescent Inorganic-Organic Hybrid Erbium Pyridine Dicarboxylate Thin Films**, ***Lukas Mai,*** Ruhr-University Bochum, Germany; *Z Giedraityte,* Aalto University, Finland; *M Schmidt, D Rogalla, S Scholz, A Wieck,* Ruhr-University Bochum, Germany; *M Karppinen,* Aalto University, Finland; *A Devi,* Ruhr-University Bochum, Germany

Erbium containing thin film materials are often used in amplifiers, detectors or LEDs because of the specific luminescence of Er^{3+} at ~1500 nm.[1] In fact, the absorption coefficient of Er^{3+} ions is too low for practical utilization. In order to enhance the luminescence, either the concentration of the erbium ions can be decreased or an organic molecule, which is sensitizing the Er^{3+}, can be used.[2] To introduce a sensing organic molecule into a thin film to produce an inorganic-organic hybrid material, exhibiting a low erbium concentration and a defined stoichiometry, the atomic/molecular layer deposition (ALD/MLD) technique is the method of choice. Here, for a complete reaction, the reactivity of the two precursors toward each other must be sufficient.[3] For the ALD of erbium oxide thin films, tris(N,N'-diisopropyl-2-dimethylamido guanidinato)erbium(III) or $[Er(DPDMG)_3]$ shows high potential, as the all-nitrogen coordinated complex exhibits a high reactivity toward oxygen functionalities.[4] In addition, it was shown that 3,5-pyridine dicarboxylic acid (3,5-PDA) can be used organic precursor in an ALD/MLD processes as a sensing ligand for the excitation of europium.[5]

Here, the successful combination of $[Er(DPDMG)_3]$ and 3,5-PDA in an ALD/MLD process is presented.[6] The usage of the guanidinate precursor resulted in high growth rates compared to common rare earth precursors, such as β-diketonates ($[Er(THD)_3]$). Furthermore, we investigated the typical ALD characteristics, including surface saturation for the applied precursors, linearity of thickness vs. cycles and an ALD window between 250 °C and 265 °C, proving a true ALD/MLD process (Figure 1). From Rutherford-Backscattering (RBS) experiments, nearly stoichiometric erbium 3,5-pyridine dicarboxylate ($[Er_2(3,5\text{-}PDC)_3]$) was found to be deposited. The thin film structure was confirmed by FT-IR spectroscopy, indicating the reaction between the precursors takes place by deprotonation of 3,5-PDA and subsequent coordination of the nitrogen functionality toward the erbium-ion. From UV-Vis investigation (Figure 2, left), a strong absorption at 270 nm was detected and assigned to the absorption of the organic molecule. Furthermore, by direct excitation of different electronic states of the erbium ions, a sharp photoluminescence emission at 1535 nm arises (Figure 2, right). Here, intensity could be increased with decreasing erbium concentration.

The obtained results show the distinct advantage of using a well-developed inorganic precursor such as $[Er(DPDMG)_3]$ in combination with different organic molecules for ALD/MLD processes in order to produce novel materials that can be precisely tailored for various applications.

2:15pm **EM+AA-MoA-4 Molecular Layer Deposition of Manganese-Ethylene Glycol Hybrid Films**, ***David Bergsman,*** *J Baker, N Yang, C MacIsaac, A Strickler, M Lillethorup, S Bent,* Stanford University

Manganese oxide films have shown potential as earth abundant catalysts for various reactions, including the oxygen evolution and reduction reactions (OER and ORR, respectively), the reduction of hydrogen peroxide, and as a promoter for the Fischer-Tropsch reaction. Because of this, many methods have been developed for depositing manganese-based materials, including incipient wetness impregnation and atomic layer deposition (ALD). However, in recent years, there has been increased effort towards the nanostructuring of materials, driven in part by the desire to increase surface-to-volume ratios, tune reaction site chemistry, and improve catalyst stability. One promising method for depositing nanostructured manganese films is hybrid organic-inorganic molecular layer deposition (MLD). By combining a metal precursor typically associated with atomic layer deposition and an organic counter reactant monomer associated with MLD, films of catalytically relevant materials can be grown with a carbon-based component that can be easily removed, allowing for further nanostructuring.

Here, we discuss the deposition of a hybrid organic-manganese film using MLD and the precursors bis(ethylcyclopentadienyl)manganese and ethylene glycol. As-deposited films are characterized using a combination of spectroscopic ellipsometry (SE), Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy (XPS) to verify the self-limiting nature of this layer-by-layer process and the successful reaction of the precursors. Time-resolved SE suggests that the organic component of the films is unstable in air over a time frame that can be controlled through the addition of a blocking layer or through chemical and temperature treatments. Characterization of the stabilized and degraded films with atomic force microscopy, scanning electron microscopy, x-ray reflectivity, and XPS show the extent of organic degradation and removal. Finally, the results of testing the manganicone films for use as a catalyst, including the OER/ORR reaction, will be discussed.

2:30pm **EM+AA-MoA-5 Synthesis, Characterization, and Electrochemistry of Molybdenum-1,2-Ethanedithiol Hybrid ALD Films**, ***Callisto MacIsaac,*** *R Closser, J Schneider, T Hellstern, D Bergsman, S Bent,* Stanford University

Hybrid atomic layer deposition-molecular layer deposition (ALD/MLD) is a self-saturating, layer-by-layer, gaseous technique for depositing thin, conformal thin films that involves both the typical metal-containing precursors used in ALD and the organic linkers of MLD. The combination of ALD and MLD chemistries enables the creation of hybrid materials that incorporate the properties and benefits of the parent materials, with the opportunity to create new electrical, magnetic, and catalytic properties. The exploration of novel gas-phase chemistries and unique new types of inorganic-organic thin films is therefore of interest both for the fundamental chemistry and for potential wide-ranging applications.

One such application is the production of hydrogen, a clean, energy-dense fuel that can be formed by the electrochemical splitting of water. Platinum is considered the ideal catalyst for the hydrogen evolution reaction (HER)

due to its low overpotential; however, it is costly and scarce. One promising substitute for platinum is MoS_2, a cheap but highly active and stable alternative whose catalytic properties are well-known. However, the HER activity of crystalline MoS_2 is limited to the exposed edge sites of the MoS_2 sheets, since the basal planes are chemically inert. This has led to the investigation of a variety of novel MoS_2 nanoarchitectures ranging from nanowires, supported nanoparticles, and 3D patterned networks in an effort to increase the number of the active edge sites relative to what is present in MoS_2 sheets. Here, we introduce a novel material that incorporates the –S-Mo-S- chemical moiety of MoS_2, yet has organic linkers that create a porous matrix for these MoS_2-like domains, as an alternative HER catalyst. Further, these organic linkers can be removed using sulfurization to introduce catalytically active edge sites.

This work investigates in detail a novel hybrid ALD-MLD process from the precursors $Mo(CO)_6$ and 1,2-ethanedithiol, with a focus on the film growth behavior and structure. Fourier transform infrared spectroscopy, X-ray diffraction, X-ray reflectivity, Raman spectroscopy, variable angle spectroscopic ellipsometry, and X-ray photoelectric spectroscopy are utilized to characterize the resultant material. This work further details proof-of-concept experiments using the Mo-ethanedithiol hybrid films as a catalyst for HER. The results show that the catalyst is active for HER, with a lower overpotential at 10mA/cm^2 and a higher current density on a geometric basis compared to flat MoS_2. The study offers insight into the possibility of other organic-inorganic materials with similar properties that can be deposited in an ALD-regime.

2:45pm **EM+AA-MoA-6 Ultrahigh Elastic Strain Energy Storage in Metal-Oxide-Infiltrated Polymer Nanopillars Generated by Infiltration Synthesis**, ***Chang-Yong Nam***, Brookhaven National Laboratory; *K Dusoe,* University of Connecticut; *A Stein, X Ye, K Kisslinger,* Brookhaven National Laboratory; *S Lee,* University of Connecticut

Infiltration synthesis is a type of inorganic-organic hybridization technique derived from atomic layer deposition, where the material precursors infiltrate into polymer medium, generating unique organic-inorganic hybrids. Here, we report the generation of an organic-inorganic hybrid nanostructure having an exceptional ability to store elastic strain energy, whose mechanical modulus of resilience for a given density exceeds what is observed in most engineering materials. Lithographically patterned polymer nanopillars with ~300 nm diameter and 1 µm height from a negative-tone resist SU-8 were subjected to the infiltration synthesis of AlO_x using trimethylaluminum (TMA) and water as precursors, creating unique composite nanopillars in which an interpenetrating polymer-AlO_x hybridized matrix extended down to ~50 nm below the surface. We performed the mechanical testing of the produced hybrid nanopillars by using an in-situ nanomechanical testing system based on a scanning electron microscope. The hybrid nanopillars after 16 cycles of AlO_x infiltration exhibited a high yield strength (500 MPa) which was accompanied by an unusually low Young's modulus (7.5 GPa) in uniaxial nanocompression tests, a unique combination of strength and modulus that has never been observed. The resulting apparent modulus of resilience, a parameter that quantifies the ability of storing elastic energy, was over 16,000 kJ/m^3, the highest among the known values. Consequently, this is translated into the specific modulus of resilience higher than most engineering materials. The infiltration-synthesized composite nanopillars combine the exceptional, tunable mechanical resilience with the compatibility with lithographic techniques, promising potential applications in micro- and nanoelectromechaical systems which require ultrahigh-elastic components for advanced actuation and sensor devices.

3:00pm **EM+AA-MoA-7 Kinetics of Vapor Phase Infiltration: Fitting Theory to Experimental Measurements**, *C Leng,* ***Mark Losego***, Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel electrical, chemical, and/or physical properties. These new materials can have applications as chemical barriers, filtration media, or photolithographic hard masks. Here, the focus is to have a better knowledge of the diffusion and reaction kinetics during this vapor phase infiltration process with the goal of understanding how both polymer structure and processing conditions can maximize the depth of inorganic infiltration. In this study, we use the model system of poly(methyl methacrylate) (PMMA) films exposed to trimethylaluminum (TMA) gaseous precursors. A basic kinetics model has been developed to describe the diffusion and reaction processes in VPI and has been fit to experimental data. From spectroscopic ellipsometry we are able o track total infiltration based upon film swelling and changes in refractive index. At a process temperature of 60°C, films are found to initially swell with the square root of time, suggesting that kinetics are dominated by Fickian-like diffusion behavior. A maximum film swelling of 60% is measured at any exposure time exceeding 1000 minutes. Using these swelling curves as a proxy for infiltration amount, we calculate effective diffusion coefficients for TMA in PMMA at 60° C to be on the order of 10^{-15} cm^2/s, with faster diffusion in PMMA films of lower molecular weight. At higher temperatures (160° C), swelling is less significant, but refractive indices of infiltrated films increase by 2% to 3%. We interpret the decrease in swelling as a result of faster chain relaxation when processing above the glass transition temperature of the polymer. To determine whether polymer films infiltrated and swollen below T_g can also undergo similar polymer relaxation behaviors, a systematic study of post-annealing was carried out at 150° C. In these instances, the amount of swelling decreases by approximately half and refractive index increases but to a lesser degree than those from the initial high process temperatures. The results of this study will be put in context with other ongoing research in the field to help build a phenomenological model that can be used to better design vapor phase processing schemes to form organic-inorganic hybrid materials.

3:15pm **EM+AA-MoA-8 Vapor Phase Infiltration for Doping Conducting Polymers**, *W Wang, F Yang,* CIC nanoGUNE, Spain; *C Chen, Y Qin,* Chinese Academy of Sciences, China; ***Mato Knez,*** CIC nanoGUNE, Spain

Vapor phase infiltration is a top-down strategy that is based on the ALD process and allows fabrication of organic-inorganic hybrid materials by incorporation of metal organic precursors into polymeric substrates. The growth of inorganic clusters or particles in the subsurface area of a polymer allows modifying some of the physical properties of the polymer greatly. While related earlier work investigated the improvement of mechanical properties of polymers applying the infiltration route, here we describe a novel approach, namely a single precursor infiltration process to dope polyaniline (PANI) or the polythiophene P3HT. The infiltration was performed with various precursors typically used in ALD processes. The conductivities were assessed with four-point probe measurements and showed significant enhancement by up to 6 orders of magnitude, confirming the efficiency of the infiltration process. Furthermore, we found that the thermal and temporal stability of the thus doped polymers were significantly enhanced in comparison to their traditionally wet-chemically doped counterparts. For example, conductivities of infiltration-doped PANI outperformthe conductivity of HCl-doped PANI if exposed to elevated temperatures (150 °C) in vacuum. In the case of P3HT, the infiltration-doped polymer maintains the gained conductivity even after exposure to ambient conditions for more than 30 days. The chemical changes resulting from the infiltration of the two polymers were characterized by FTIR and Raman spectroscopy and will be discussed. SEM micrographs showed that the morphologies of the samples did not alter after the infiltration process, being one of the most important arguments for doping conductive polymers in the presented way.

4:00pm **EM+AA-MoA-11 Catalysts Modified by ALD for Harsh Biomass Conversion Processes**, ***Steven Christensen***, *K Hurst, M Griffin, D Vardon,* National Renewable Energy Laboratory

Black liquor, fast pyrolysis, and bio-coke are terms that denote some of the challenges encountered from the feedstock, processes, and unwanted products of catalytic biomass conversion that ALD techniques can address. Catalysts developed for the petroleum industry often deactivate and degrade when applied to biomass applications. Furthermore, biomass can offer chemicals and fuels that cannot be derived from petroleum feedstock and therefore new catalyst formulations and properties are required. Research of catalytic materials for biomass conversion at the National Renewable Energy Laboratory is using ALD to reduce metal leaching, improve de-oxygenation catalysis, and tailor catalysts with novel properties. An overview of the challenges for biomass processing and strategies for how ALD catalysts can be designed to solve these problems will be presented. The production of bio-nylon precursors and catalytic fast pyrolysis of bio-oil will be used as examples. Advanced catalysts from ALD look to have an exciting future to help enable new technologies for this industry.

4:15pm **EM+AA-MoA-12 Effects of Alumina Incorporation by Particle Atomic Layer Deposition on Sintering and Microstructure of Yttria-Stabilized Zirconia (8YSZ)***, **Christopher Bartel**, R O'Toole, M Kodas, A Drake, A Horrell,* University of Colorado - Boulder*; R Hall,* ALDNanoSolutions, Inc.*; C Musgrave, A Weimer,* University of Colorado - Boulder

Yttria-stabilized cubic zirconia (YSZ) is the most-common electrolyte material for solid oxide fuel cells (SOFC) due to its reasonable oxygen-ion conductivity and chemical stability across a wide range of environments. To achieve suitable ionic conductivity, YSZ electrolytes must be near theoretical density; this necessitates high sintering temperatures, often exceeding 1450 °C. This high sintering temperature limits the viability of low-cost one-step sintering during manufacturing and thus increases the cost of SOFC fabrication. Previous researchers have successfully lowered the required YSZ sintering temperature through incorporation of aluminum oxide (Al_2O_3) particles with the YSZ. While this technique has proven to be successful in reducing the sintering temperature, the presence of particulate Al_2O_3 inclusions in densified parts reduces the homogeneity of the electrolyte which may have deleterious effects on operation. In this work, we report on the use of atomic layer deposition (ALD) to precisely and conformally coat individual YSZ particles with the desired amount of Al_2O_3. Constant-rate-of-heating (CRH) experiments were conducted using a horizontal push-rod dilatometer to extract the activation energy of sintering in the initial stage and also gain mechanistic insights into the active diffusion mechanisms as a function of ALD film thickness. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to characterize the as-deposited thin Al_2O_3 films and the effects of the Al_2O_3 films on grain growth and microstructure during densification. Al_2O_3 incorporation by ALD is shown to have unique phenomenological effects on the densification of YSZ as compared with conventional Al_2O_3 incorporation using particle-based approaches.

4:30pm **EM+AA-MoA-13 Low-Temperature ALD Cobalt Sulfide for High-Efficient Hydrogen Evolution Textiles***, **Donghyun Kim**, J Park, H Kim,* Yonsei University, Republic of Korea

Hydrogen energy is promising energy source, because it is sustainable and renewable green energy alternatives for fossil fuels and coal. The key component for producing hydrogen in water is the catalyst for hydrogen evolution reaction (HER).

To increase HER efficiency, maximizing surface area for reaction is important factor. Complex structure is widely used to meet this requirement. For example, conducting substrate based on nanowire, nickel foam, or carbon nanotube would serve as electron transfer template. However, these conventional substrates for HER limit its applicable area such as flexible devices. To overcome the limit, conducting textile could be adequate substrate for HER. Textile is intensively used as form of fabric, and it can be applied from clothes to massive energy storage system.

Up to now, the noble metal including Pt is considered as the best electrocatalyst for HER with low overpotential, tafel slope and high exchange current density. However, the noble metal is extremely expensive so that catalyst based on earth-abundant materials with high-efficiency are required. Transition metal chalcogenides (TMCs) have attracted attention owing to its superior catalytic properties. Due to the electron configuration of TMCs, outermost *d* orbitals of TMCs make electron transfer easy. Especially, metallic TMCs including cobalt sulfide, vanadium sulfide, 1T-molybdenum sulfide shows superb electrochemical properties due to their high conductivity which promotes transport of electrons.

In this study, the cobalt sulfide (CoS_x) was synthesized using atomic layer deposition (ALD). ALD is the self-limited process based on surface reaction so that the CoS_x could be deposited with excellent uniformity, precisely controlled thickness in large area. The characteristics of deposited ALD CoS_x were analyzed using XPS and XRD. The morphology and thickness of the film were observed using SEM and AFM and finally, the electrocatalyst based on cobalt sulfide could be synthesized. It showed low tafel slope (~ 41 mV/dec) comparable to the value of Pt, and low overpotential. Also, conducting textiles could be utilized as template for HER catalyst due to the low-temperature process of ALD. As the result, the ALD CoS_x can be considered as the promising electrocatlayst for HER as promising candidate for replacement of Pt.

4:45pm **EM+AA-MoA-14 Atomic Layer Deposition of Platinum: An Avenue to the Scalable Synthesis of Ultra-low-loading Fuel Cell Catalysts?***, A Goulas,* Delft IMP B.V., Netherlands*; F Grillo, A Dokania,* Delft University of Technology, Netherlands*; D Valdesueiro,* Delft IMP B.V., Netherlands*; H Van Bui,* Delft University of Technology, Netherlands*; **Bart van Limpt**,* Delft IMP B.V., Netherlands*; J Moulijn, J van Ommen,* Delft University of Technology, Netherlands

We present an approach for tailoring the growth of platinum nanostructures on commercially-available carbon black powder (Vulcan XC72) based on atomic layer deposition (ALD) in an atmospheric-pressure fluidized bed reactor. By varying the number of ALD cycles, the metal loading could be effectively controlled in the 2 – 10 wt.% range. The expansion of the ALD processing window into lower deposition temperatures, enables us to steer the Pt growth towards highly-dispersed nanoparticles with narrow size distributions.

Although one does not simply control the NP size by the number of ALD cycles, here, by using atmospheric-pressure ALD in a fluidized bed reactor we could use the temperature as another knob to tailor the size distribution. In particular, by employing low deposition temperatures we could achieve narrow size distributions while maximizing the inter-particle distance.

5:00pm **EM+AA-MoA-15 Pd-Ag Bimetallic Nanograin-Decorated Nylon Nanofibers: Efficient Catalytic Reduction of 4-Nitrophenol***, K Ranjith, A Celebioglu,* Bilkent University, Turkey*; H Eren,* Delft University of Technology, Netherlands*; N Biyikli,* Utah State University*; **Tamer Uyar**,* Bilkent University, Turkey

Reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride catalyzed by both monometallic and bimetallic nanostructures through hydrogenation process is of utmost interest. By constructing the bimetallic functionality on a support or template has attracted much attention over the points of catalytic interaction and stability. We demonstrate an effective synthesis process of creating the Pd-Ag bimetallic functionality on the Nylon nanofibers by combining the atomic layer deposition (ALD) of Pd nano grains followed by the solution chemical reduction of Ag ions to form the Pd-Ag bimetallic nanograin alloys. Through the ALD process, the size, density and monodispersivity of the Pd nanoparticles were controlled and reflected as nucleation sites for the loading of Ag ion with controllable ratio. The evolution of the catalytic activity through the reduction of 4-nitrophenol to 4-aminophenol improved on constructing the bimetallic functionality which betters the selectivity of p-nitrophenol adsorbate to the catalytic surface as predicted by Brønsted−Evans−Polanyi (BEP) relation. Different composition ratio of the Ag ion with the bimetallic functionality with ALD Pd nano grains initiates the understanding of the electronic and geometric effect exhibited by the role of Ag ion at the Pd interface. Additionally, Pd nanograins act as nucleation platform for the Ag ion loading, which reveal the absence of sole decoration of Ag ions on the nylon fiber surface. The reduction rate was significantly higher for the Pd-Ag bimetallic alloys loaded nylon fibers relative to the Ag and Pd decorated Nylon fibers which evidence the electronic promotion of Pd ions through the Ag ion which results in the improved catalytic behavior. This observation attributes to the simultaneous effect of (i) enhancive surface area for the interaction through the template form, (ii) supportive high interactive crystallographic facets for the catalytic reduction, and composition of the bimetallic nanostructures. The template based catalyst shows the use of recoverable and reusable performance without obvious loss on catalyst and activity after 3 consecutive cycles.

5:15pm **EM+AA-MoA-16 Size-Selective Catalysts with an Ultra-Thin Porous Shell Prepared by Molecular Layer Deposition***, **Zeyu Shang**, X Liang,* Missouri University of Science and Technology

Heterogeneous catalysts are widely used due to many advantages, including the ease of separating the catalysts by filtration after reaction. However, heterogeneous catalysts usually cannot selectively convert specific molecules in a reactant mixture to only desired products. Size-selective catalysis is an important concept for improving the selectivity of heterogeneous catalysts. In most previous studies, unsupported and nonporous substrates supported metallic nanoparticles were encapsulated in relatively thick porous structures to realize the size-selectivity of heterogeneous catalysts by the size discrimination effect of the porous shell. However, the catalytic activity of the catalysts greatly decreased due to mass transfer limitations brought by relatively thick shells and the contact areas between the porous shells and active sites. In our study, we deposited an ultra-thin porous oxide shell on high surface area substrate-supported Pt nanoparticle catalysts, using molecular layer deposition

(MLD), followed by oxidation to remove the organic components in hybrid organic/inorganic MLD films. The encapsulated catalyst showed very high selectivity in catalyzing hydrogenation reactions of n-hexene over cis-cyclooctene. However, there was a decrease of the catalytic activity due to contact areas between the porous shell and metallic nanoparticles. To reduce the contact areas, we introduced gaps between the Pt nanoparticles and porous shells using a sacrifical layer of self-assembled monolayers (SAMs) on the Pt nanoparticles, before the deposition of a MLD layer. This novel nanostructured catalyst showed much higher activity, as compared to the catalyst that had been directly coated with the MLD layer.

Emerging Materials
Room Plaza Exhibit - Session EM-MoP
Emerging Materials Poster Session

EM-MoP-1 ALD of Copper(I) Halide Direct Bandgap Semiconductors, *T Homola, R Krumpolec, **David Cameron,*** Masaryk University, Czech Republic; *R Zazpe, J Přikryl, J Macák,* University of Pardubice, Czech Republic; *P Maydannik,* Lappeenranta University of Technology, Finland; *G Natarajan,* Indira Gandhi Centre for Atomic Research, India

Zinc blende-structure copper(I) halide materials (CuHa) are direct gap semiconductors with band energies in the ultra-violet region. They have high exciton and bi-exciton binding energies which have the potential for laser action with very low lasing threshold. Thin films and nanocrystallites of CuHa have been deposited by evaporation, sputtering and molecular beam epitaxy. Recently, preliminary work has shown that ALD has the ability to deposit thin films and nanocrystallite arrays which exhibit the characteristic photoluminescence of zinc blende CuCl. This paper investigates the growth processes and crystal structure and shows that CuCl films can be grown within an ALD window which ranges from 50°C to 150°C using [bis(trimethylsilyl)acetylene] (hexafluoroacetylacetonato)-copper(I) and HCl in butanol as Cu and Cl precursors, respectively. Initial nucleation depends on the length of the post-Cl purge times with short purge time leading to faster nucleation. After nucleation the deposition rate is similar in both cases.

In addition, the results of film deposition of CuCl and CuBr using alternative halogen precursors will be presented. The use of *in-situ* deposition of capping layers to prevent degradation of the CuHa due to atmospheric moisture and their effect on the stability and structure of the films will be described.

EM-MoP-2 Atomic Layer Deposition of Topological Insulator Selenides and Tellurides, ***Tommi Tynell,*** *C Wiegand, A Thomas, K Nielsch,* Leibniz Institute for Solid State and Materials Research Dresden (IFW Dresden), Germany

Group V-VI chalcogenides based on the tellurides and selenides of Bi and Sb are well known for their thermoelectric properties, but they also display topological insulator behaviour, characterised by strong spin-orbit coupling and conducting surface states taking the shape of a Dirac cone. Topological insulators display a number of interesting properties, and the fact that carriers in the surface states have their spin orientation locked to their momentum can be particularly useful for applications in the field of spintronics. Developing a process for depositing high-quality thin films of these materials is a priority in their experimental study, because it would enable the observation of the topological surface states without too much influence from unwanted bulk carriers. Epitaxial growth of Bi_2Te_3 has been achieved using MBE [1] and PLD [2], and ALD processes have also been developed for the V-VI chalcogenides [3-5]. However, issues remain with the surface quality of some ALD-deposited chalcogenide films. Namely, flaking of the surface has been observed [4,5], making the proper investigation of surface states impossible. Thus, developing an ALD process where the surface issues can be avoided is imperative for investigating the topological insulator properties of chalcogenide thin films.

In this work, Sb_2Te_3, Sb_2Se_3 and Bi_2Se_3 films have been deposited using chloride precursors for Sb and Bi, and alkylsilyl precursors for Te and Se. A variety of substrates, including (100) Si, (111) Si and (0001) sapphire have been utilised, and the influence of the deposition temperature as well as the pulsing and purging times have been investigated. The film growth, structure and surface characteristics have been analysed using x-ray reflectivity, x-ray diffraction and scanning electron microscopy.

[1] Y-Y. Li *et al.*, *Adv. Mater.***2010**, 22, 4002-4007.

[2] S. X. Zhang *et al*., *Thin Solid Films***2012**, 520, 6459-6462.

[3] S. Zastrow *et al.*, *Semicond. Sci. Technol.***2013**, 28, 035010.

[4] T. Sarnet *et al.*, *J. Phys. Chem. A***2015**, 119, 2298-2306.

[5] T. Sarnet *et al.*, *J. Mater. Chem. C***2015,** 3, 4820-4828.

EM-MoP-3 New precursor for low temperature deposition of SiO_2 layer using thermal and plasma enhanced ALD techniques, *A Korolev, **Hima Lingam**, V Chitturi, P Cobb,* Nova-Kem; *M Boleslawski, D Suh, C Choi, H Jeong,* Wonik Materials

A new precursor for deposition of SiO_2 layers at substrate temperatures below 200 °C (VLTO1) has been developed recently at Nova-Kem. It is a sufficiently volatile liquid having a vapor pressure of 1 torr @ 75°C and thermally stable up to 200 °C. In a series of thermal and plasma enhanced ALD experiments (using O_3 and O_2 as oxidizers respectively) it has demonstrated excellent growth rate of 1.0 – 1.7 Å/cycle in the Si substrate temperature range of 50 – 150 °C. The highly uniform blanket SiO_2 films deposited by both methods exhibit high chemical purity, good Si:O stoichiometry and density, acceptable leakage current parameters and *k* values ranging between 4.3 and 4.9. The presented results favor VLTO1 in comparison with the leading low temperature SiO_2 precursors. A comparison of theoretically calculated parameters for VLTO1 and other known SiO_2 precursors is also discussed.

EM-MoP-4 Modeling of the Reactions of Hexachlorodisilane on NH and NH_2 Functionalized Silicon Nitride Surface, *X Wang,* The Dow Chemcal Company; ***Xiaobing Zhou***, *B Hwang,* The Dow Chemical Company; *B Ketola, B Rekken, T Sunderland, A Millward, M Telgenhoff, V Shamamian, C Lee, Y Ahn, W Chung,* The Dow Chemcal Company

Chloro(di)silanes deposit silicon nitride films with ammonia co-reactant in either a thermal or plasma enhanced atomic layer deposition (ALD) process. The film growth involves alternate silylation and ammonolysis reactions. We have studied the silylation reactions of hexachlorodisilane (HCDS) on an NH and NH_2 functionalized silicon nitride (SiN) surface with density functional theory (DFT). The modeling suggests that the cleavage of the Si-Cl bonds in HCDS by the surface NH_2 groups has a 44.4 kcal/mol energy barrier that is substantially lower than the energy barriers for the cleavage of the Si-Si bond by the surface NH_2 groups and the cleavage of either the Si-Cl or Si-Si bond by the surface NH groups.

EM-MoP-5 New Silicon precursor for Low Temperature SiN_x ALD Applications, *A Korolev, H Lingam,* ***Venkateswara Chitturi,*** Nova-Kem; *M Boleslawski, C Choi, H Jeong, D Suh,* Wonik Materials

Silicon precursors for deposition of atomically-thin SiN_x layers at temperatures below 200 °C are of high interest in the microelectronic industry. We have evaluated several silicon precursors for potential SiN_x ALD using Schrodinger software suite and identified a new precursor (VLTN-1) that has a low Si-X bond dissociation energy as well as low activation energy for the dissociative chemisorption step. These theoretical properties favor VLTN-1 in comparison with known SiN_x precursors such as hexachlorodisilane, octachlorotrisilane, and diisopropylaminosilane. The new precursor has been experimentally synthesized, and its thermal properties were evaluated using TGA methods. The results of VLTN-1 deposition experiments are also presented.

EM-MoP-6 Structure and Growth Behavior of MLD Films Using Cyclic Azasilanes, Maleic Anhydride, Trimethylaluminum and Water, ***Ling Ju,*** *N Strandwitz,* Lehigh University

Molecular layer deposition (MLD) is used to grow hybrid organic-inorganic films. We reported a four-step MLD ABCD sequence using N-(2-aminoethyl)-2,2,4-trimethyl-1-aza-2-silacyclopentane (AZ), maleic anhydride (MA), trimethylaluminum (TMA), and H_2O and a three-step ABC sequence consisting of AZ, MA and H_2O.[1] The growth rate of the ABC sequence increased to 90 Å/cycle after approximately 50 cycles, indicating precursor diffusion into the films during deposition.

Based on these results, additional quartz crystal microbalance (QCM) data have been acquired during individual reactions, and provide detailed information of precursor diffusion behavior, such as diffusion coefficient and diffusion depth of different precursors. Ellipsometric porosimetry and X-ray reflectivity (XRR) measurements estimate the density and porosity of the as-deposited films, as well as their structural evolution during annealing process. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) suggest the differences in functionalities and chemical composition between the ABC and ABCD films, providing evidence for the reaction mechanisms and diffusion behavior. These studies provide better understanding of the structures and growth behavior of the MLD films, and avenues for basic studies of the effects of specific chemical functionalities on growth.

1 L. Ju, B. Bao, S. W. King and N. C. Strandwitz, J. Vac. Sci. Technol. A **35,** (2017).

EM-MoP-7 Divalent Group IV Precursors for Atomic Layer Deposition Features, *M Nim,* ***Hyunkee Kim,*** *K Mun, J Park, J Park,* Hansol Chemical, Republic of Korea

Recently, interest of group IV precursors with wide ALD window has increased for their application of semiconductor industry and flexible display. Especially, formation of encapsulation layer for gas barrier and transparent conducting oxide for electrode in flexible display application

require Si and Sn precursors with low deposition temperature. In this work, we report divalent Group IV precursors with liquid phase at ambient temperature. Three new precursors were characterized by NMR and viscometer. Their vaporization characteristics and thermal stabilities were also investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). All the precursors showed to be effective precursors for thermal ALD of oxide thin films with O_3 as an oxidant gas and demonstrated wide ALD window in the range of 100 ℃ to 320 ℃.

EM-MoP-8 Plasma Enhanced Atomic Layer Deposition of Aluminium Sulphide*, **Jakob Kuhs**, Z Hens, C Detavernier,* Ghent University, Belgium

Recently, there has been much interest in metal sulphides due to their relevance for energy, photonics and micro electronics applications. Since many of the targeted devices like e.g. field effect transistors, solar cells and transparent conducting films require uniform coatings with precise thickness control, Atomic Layer Deposition (ALD) is an ideal deposition technique.

Aluminum sulphide has a number of promising applications. It can be implemented as an interface layer between high-k dielectric and a III-V semiconductor surface in field effect transistors. It can also be used as a lithium ion conductor for solid state batteries. Furthermore a thorough understanding of the ALD process of Al_2S_3 is crucial in order to realise ALD of Al doped zinc sulphide (ZnS:Al) which may have application as an n-type transparent conducting film. Until now this is done mostly by Electron-Beam Deposition, solution growth methods or CVD.

While thermal ALD of Al_2S_3 from trimethylaluminium (TMA) and hydrogen sulfide (H_2S) were already reported, to the best of our knowledge, no plasma enhanced ALD processes of Al_2S_3 were reported until now.

Here we report on a plasma enhanced ALD process for Al_2S_3. Thin films were deposited in a home-built pump-type ALD reactor by using TMA in combination with argon diluted H_2S-plasma as reactants. The substrates were Si(100) wafers covered with native SiO_2. Argon diluted H_2S-Plasma was used instead of a pure H_2S-Plasma in order to minimize the exposure of the ALD reactor to the highly reactive sulphur radicals. The plasma was generated remotely from the substrate by RF inductive coupling at 200 Watt. The substrate temperature was varied from 100°C to 500°C. Thin film growth rate was monitored in-situ by spectroscopic ellipsometry while the structural properties and composition were characterised ex-situ using X-ray diffraction, X-ray fluorescence, X-ray reflectivity, X-ray photoelectron spectroscopy and energy-dispersive X-ray spectroscopy.

Despite existing reports on thermal ALD using TMA and H_2S, no growth could be achieved with this process in our reactor. However, using a H_2S/Ar-plasma instead of the H_2S gas resulted in a linear growth after a short nucleation time (Fig. 1). The growth per cycle (GPC) of the plasma enhanced ALD process was 1.1 Å/cycle at a deposition temperature of 100°C and decreased down to 0.1 Å/cycle at a deposition temperature of 500°C (Fig. 2). Saturation of the ALD process was observed for TMA and H_2S/Ar-plasma pulse times both longer than 4s (Fig. 3). The obtained Al_2S_3 thin films were amorphous as deposited. From EDX analysis a ratio of approximately 2:3 between aluminium and sulphur was confirmed.

EM-MoP-9 The Film Property of Super-cycled Al_2O_3/SnO_x Atomic Layer Deposition and the Associated Thin Film Transistor Performance*, **Seung-Hwan Lee**, S Choi,* Hanyang University, Korea*; J Park,* Hanyang University, Republic of Korea

Crystalized SnO_2 is known as superior transparent conducting oxide (TCO) which could be used in application such as displays, solar cells and sensors. It can be achieved to attain higher TCO performance by doping other groups and one of them is aluminum dopant. By controlling Al contents in SnO_x matrix, the physical and optical properties was easily manipulated in atomic layer deposited aluminum tin oxide (ATO) layers, which were used with tetrakis(dimethylamino)tin (TDMAT) as a Sn precursor, trimethylaluminum (TMA) as an Al precursor and hydrogen peroxide (H_2O_2 30%) as a reactant. As Al_2O_3 and SnO_x cycles are mixed with various super-cycles (Al_2O_3:SnO_x=n:m), the film properties were systematically changed in terms of the crystallinity, growth rate, and refractive index. The growth rate and refractive index were varied from 1.9 Å/cycle/2.05 to 1.1 Å/cycle/1.63, respectively. Interestingly, it suggested that the inserted TMA molecule or deposited Al2O3 layer affected to suppress initial growth significantly. The film crystallinity was changed from tetragonal SnOx to amorphous like ATO as the Al contents increased in SnOx matrix. Also, as modulating the syper-cycled Al2O3/SnOx layers, the electrical properties of ATO films can be controlled form conductor to semiconductor easily. Consequently, this presentation will show the suitable ATO semiconductor boundary and the associated thin film transistor performance.

EM-MoP-10 Optical Properties and XPS Analyses of $Ti_xSi_{(1-x)}O_2$ Films Prepared by ALD and Comparison to ab-initio Predictions*, **Marek Elias**,* CEITEC, Brno University of Technology, Czech Republic*; P Ondracka,* Masaryk University, Czech Republic*; D Necas,* CEITEC, Masaryk University, Czech Republic*; J Vida,* Masaryk University, Czech Republic*; E Kedronova, L Zajickova,* CEITEC, Masaryk University, Czech Republic

$Ti_xSi_{(1-x)}O_2$ films with varied Ti:Si ratio were prepared by atomic layer deposition (ALD) combining cycles with tetrakis(dimethylamido)titanium and tris(dimethylamino)silane for Ti and Si monolayers, respectively, with oxidizing step. The process was enhanced by plasma and the substrate temperature was 250 °C. The films were characterized by optical spectroscopic methods (either reflectometry or ellipsometry) in wide spectral range from 0.56 to 10.3 eV and all the experimental data were fitted by dispersion model based on the parametrization of the joint density of states for valence-to-conduction interband transitions. The chemical composition and bonds were investigated by X-ray photoelectron spectroscopy. The results on the optical properties and chemical structure were compared to the films prepared by plasma enhanced CVD obtained also with varied Ti:Si ratio. Density functional theory was used to predict optical properties and binding energies of core electrons sensitive to chemical environment in $Ti_xSi_{(1-x)}O_2$ amorphous materials.

EM-MoP-11 Atomic Layer Deposition of MoO_x:N films: Electrical and Electrochemical Properties*, **Arpan Dhara**, D Saha, S Sarkar,* Indian Institute of Technology Bombay, India

Oxynitrides or nitrogen incorporated oxides of transition metals are rapidly gaining attention in materials research because of their tunable electrical and optical properties. They offer usage in variety of applications like photocatalysis, phosphors, electrochemical energy storage, magnetic materials etc. Primary changes in the material properties after incorporation of nitrogen occur due to the difference in electronegativity, electronic charge and polarizability between oxygen and nitrogen atoms. However, effective and homogeneous doping in the host material is a major practical issue till date. Constructive ways to increase the conductivity without significantly altering the material's chemical properties after doping are still a challenge. Usually nitrogen doping is carried out by annealing oxides under NH_3 or N_2/H_2 gas environment. In such circumstances the metal ions are sensitive to reduction which results in the formation of undesirable phases in the doped materials. Also the possibility of dopant inhomogeneity is a major drawback towards obtaining good quality doped materials.

Here we report, amorphous nitrogen-doped molybdenum oxide (MoO_x:N) thin films synthesized by atomic layer deposition (ALD) at relatively lower temperature of 170^0C. One ALD cycle of molybdenum nitride (MoN_x) is sandwiched for nitrogen incorporation between two MoO_x layers. The concentration of nitrogen is controlled by varying the ratio of MoO_x/MoN_x layers. Quartz crystal microbalance (QCM) measurement is carried out to study the mass change after every single precursor dosed into the reactor. Secondary Ion Mass Spectra **(**SIMS) shows the presence of nitrogen throughout the deposited films. Hence uniform doping is adequately achieved at the reaction temperature. It is observed that conductivity of MoO_x films increase with increase in nitrogen doping concentration. Room temperature and low temperature electrical properties of different films are also studied in detail to understand the transport mechanism with and without nitrogen incorporation.

Both doped and undoped MoO_x are deposited on high surface area MWCNTs and applied as anode material in lithium ion batteries. As expected, doped electrodes show improved performance because of the better ionic and electronic conductivity.

EM-MoP-12 *In Situ* Characterization of Thin Film Molybdenum Carbide using Spectroscopic Ellipsometry*, **Adam Bertuch**,* Ultratech*; J Hoglund,* SemiLab*; L Makai,* Semilab*; J Byrnes,* SemiLab*; J McBee, G Sundaram,* Ultratech

Molybdenum carbide (MoC_x) is an extremely hard transition metal carbide with demonstrated super conductive behavior. Thin film, two-dimensional (2D) molybdenum carbide in a synthesized state with a surface termination group called MXenes has been shown to exhibit either conducting or semiconducting properties and has been identified as a potential thermoelectric material. Synthesis and de-lamination techniques have been demonstrated for 2D Mo_2C by Hamlin *et al*.[1]

In this work we characterize the growth mechanism for depositing the first few cycles of plasma enhanced atomic layer deposition (PE-ALD) MoC_x film with the goal of achieving atomically thin continuous MoC_x. PE-ALD grown MoC_x has been demonstrated using $(^tBuN)_2(NMe_2)_2Mo$ with H_2 plasma at

150 °C.[2] This deposition technique will be explored in greater detail using real time *in situ* spectroscopic ellipsometry (SE) with a wavelength range from 245 to 990 nm. The nucleation and initial film growth rates can be measured through each PE-ALD half cycle reaction to determine and evaluate the mechanism of growth occurring at the film to substrate interface.

References

[1]J. Hamlin et al., Adv. Funct. Mater. **26,** 3118 (2016).

[2]A. Bertuch, B Keller, N. Ferralis, J. C. Grossman, and G. Sundaram, J. Vac. Sci. Technol. A **35,** 01B141 (2017).

EM-MoP-13 Molecular Layer Deposition of Boron Carbide from Carboranes*, **Michelle Paquette**, L Dorsett, S Malik, A Caruso,* University of Missouri-Kansas City*; J Bielefeld, S King,* Intel Corporation

Atomic layer deposition (ALD) research has exploded in this era of electronic miniaturization, smart materials, and nanomanufacturing. To live up to its potential, however, ALD must be adaptable to many types of materials growth. To extend the reach of this layer-by-layer deposition framework, researchers have begun to explore molecular based processes. Still relatively rare, existing molecular layer deposition (MLD) processes are typically based on the condensation of “linear” 2D or “brush-type” organic polymer chains. To move toward a 3D MLD growth model, precursors with multiple reaction sites would be desirable. To this end, icosahedral carborane ($C_2B_{10}H_{12}$) molecules provide an interesting target. Carboranes have been used in the plasma-enhanced chemical vapor deposition of boron carbide films for low-*k* interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules, wherein the terminal H atoms at each vertex are known to be labile in the presence of plasma, heat, or a number of chemical reagents. The carborane molecule is very stable and can be derivatized with a range of functional groups; dozens of these derivatives are available commercially, many of which have relatively high vapor pressures. As such, the carborane molecule is particularly intriguing as a novel MLD precursor for 3D growth, possessing unique symmetry, chemical reactivity, and volatility properties not commonly encountered in traditional organic molecules. In this contribution, we describe early work in our group toward developing a novel MLD process for the growth of boron carbide films using a number of different carborane precursors and substrates.

EM-MoP-14 Sub-10 nm Scalable Hybrid Dielectric Engineering on MoS_2 for 2D Materials Based Devices*, **Lanxia Cheng**, J Lee, H Zhu, A Ravichandran, Q Wang, A Lucero, M Kim, R Wallace,* University of Texas at Dallas*; L Colombo,* Texas Instruments, USA*; J Kim,* University of Texas at Dallas

Successful realization of high-performance 2D-based devices requires integration of high quality dielectric film as surface passivation and current barrier. Using atomic layer deposition combined with surface pre-treatments, several studies have demonstrated the downscaling of high-k dielectrics to a few nanometers with promising properties. However, besides inorganic dielectrics, integration of organic-inorganic hybrid dielectric films on MoS_2 using MALD has been rarely investigated, which provides an alternative way of engineering dielectrics with excellent scalability, tunable film compositions, and controllable chemical and electronic properties.

In this work, we explored the deposition of low-k organic-inorganic OTS-Al_2O_3 or OTS-TiO_2 hybrid dielectric films on MoS_2 by molecular atomic layer deposition (MALD). With the assistance of reactive ozone species, our hybrid films demonstrated a controllable thickness scalability at a growth rate of 0.55 nm/cycle with excellent uniformity as verified by the AFM and HR-TEM images. The interfacial chemical composition and lattice structure characterization using XPS and Raman also show undetectable interfacial oxidation states and structural disordering on the MoS_2 surface, owing to its better chemical stability towards ozone exposure. Additionally, our XPS valence band and loss features analysis suggest a tunable band alignments of the MALD hybrid films by replacing the inorganic Al-O component with Ti-O, which also increase the film dielectric constant from 4.5 to ~7.8. Electrical results of top gated MoS_2 devices suggest that these MALD films have promising electrical properties, such as low leakage current (~10^{-5} A/cm^2), minimal doping and small hysteresis of ~40 mV at zero back-gate voltage. Our experimental findings have provided a low cost and reproducible way of fabricating scalable hybrid films on TMDs as gate tunneling dielectrics promising for 2D devices and flexible electronic applications.

We acknowledge partial financial support from the Southwest Academy on Nanoelectronics (SWAN) by the Nanoelectronic Research Initiative and NIST; and the NRF (No. 2015M3D1A1068061) in Korea, and TMEIC for providing the ozone generator.

EM-MoP-15 Critical Layer Thickness Determination for GaN Thin Films Grown on Sapphire Substrate via Hollow-Cathode Plasma-assisted Atomic Layer Deposition*, **Mustafa Alevli**, N Gungor,* Marmara University*; N Biyikli,* Utah State University

Device quality epitaxial GaN films require substrate temperatures typically higher than 600°C. However, with recent efforts using plasma-assisted atomic layer deposition, crystalline GaN films with preferred crystal orientation were obtained at substrate temperatures as low as 200°C. In this study, we report on the optical and structural properties of highly oriented (002) GaN with different thicknesses, ranging from 5 nm to 100 nm deposited via hollow-cathode plasma-assisted ALD (HCPA-ALD) on c-plane sapphire substrates. Although the compressive stress is a result of lattice mismatch between GaN films and substrate, it has been reported that the average strain in GaN thin films strongly correlates with the film thickness and usually changes from compressive to tensile as thickness increases. In the present research, the evolution of the average strain, phonon positions, Bragg reflection positions, and optical band gap energy in HCPA-ALD-grown GaN films have been analyzed. The XRD scans of all GaN samples revealed that the films are crystalline with hexagonal wurtzite structure. The films have been characterized from the mid-infrared to the ultraviolet spectral range by using spectroscopic ellipsometry in order to obtain the critical optical parameters including optical band edge and refractive index which helped us to understand the influence of film thickness on the aforementioned parameters. The measurements indicate that the increasing trend of the refractive index (n) reverses around ~60 nm. However, we have not observed a clear correlation between optical band gap and film thickness. The lowest optical band edge values obtained from ellipsometry is ~3.56 eV. Phonon modes in GaN films were studied by employing both Raman and infrared spectroscopic ellipsometry.

The E_1(TO), E_1(LO), A_1(TO), A_1(LO) and E_2(high) phonon modes were identified for all four samples. All the phonon peaks related to GaN are considerably blue shifted with respect to their bulk values. This particular behavior is similar to the ones observed in GaN quantum dots. The E_1(TO) and A_1(LO) phonon modes are following comparable trend where the phonon peak positions shift towards lower wavenumbers for increasing thickness up to ~60 nm, while the phonon peak positions move towards the bulk value for 100 nm film. E_2(high), E_1(TO), and A_1(TO) vibrational Raman peaks ranging from 500-600 cm^{-1} are difficult to separate, while the trending Raman peaks appear to evolve very strongly with thickness which is an indication of improving crystalline quality. The overall results suggested that GaN films with thicknesses above 60 nm feature different behavior compared to thinner GaN films.

EM-MoP-16 Digital Doping of ALD VO_2 for Thermochromic Applications*, **Alexander Kozen**, M Currie,* U.S. Naval Research Laboratory*; K Jungjohann,* Sandia National Laboratory*; B Downey,* U.S. Naval Research Laboratory, usa*; C Eddy, Jr., V Wheeler,* U.S. Naval Research Laboratory

Vanadium Dioxide (VO_2) is an interesting thermochromic material that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 68˚C. This structural phase transition is accompanied by major changes in electrical and optical properties, particularly in the infrared. As such, VO_2 is suitable for many applications including microbolometers, adaptive thermal coatings, and passive spacecraft thermal shielding.

While the T_c of VO_2 is convenient for many applications, it is desirable to modify the T_c to other values for either new applications or improved performance in the previously stated applications. The T_c of VO_2 is known to be strain-mediated.[1] Strain in VO_2 has been induced via deposition of thin films onto lattice mismatched epitaxial substrates, as well as by doping with other transition metal elements besides V.[2], [3]

For the first time, we are investigating doping of ALD VO_2 using other elements such as Al, Ti, Nb, and W by incorporation of their oxides into the binary ALD VO_2 process (TEMAV + O_3). We will discuss the fundamentals and limitations of doped ALD VO_2 growth and basic materials characterization, and will demonstrate the impact of dopant concentration and identity on the phase transition properties (both optical and electrical) of the resulting films.

Generally, inclusion of dopants such as Ti and Al into the ALD VO_2 process in amounts between 1% and 10% results in surfactant-like film growth behavior, with increasing dopant concentrations reducing RMS roughness of the ALD films from ~2 nm to ~0.2 nm. Higher concentrations of dopants also interfere with film crystallization, inhibiting the magnitude of the metal-insulator transition. Smaller concentrations of dopants can modify

the T_c of the VO_2 films either up or down, depending on dopant identity and concentration.

[1] J. M. Atkin, S. Berweger, E. K. Chavez, M. B. Raschke, J. Cao, W. Fan, and J. Wu, "Strain and temperature dependence of the insulating phases of VO 2near the metal-insulator transition," *Phys. Rev. B*, vol. 85, no. 2, pp. 020101–4, Jan. 2012.

[2] W. Burkhardt, T. Christmann, B. K. Meyer, and W. Niessner, "W-and F-doped VO 2 films studied by photoelectron spectrometry," *Thin Solid Films*, vol. 345, no. 2, pp. 229–235, 1999.

[3] X. Wu, Z. Wu, C. Ji, H. Zhang, Y. Su, Z. Huang, J. Gou, X. Wei, J. Wang, and Y. Jiang, "THz Transmittance and Electrical Properties Tuning across IMT in Vanadium Dioxide Films by Al Doping," *ACS Appl. Mater. Interfaces*, vol. 8, no. 18, pp. 11842–11850, May 2016.

EM-MoP-17 Characterization and Comparison of ALD Laminate Structures with HfO_2 + SiO_2 as MIM Capacitor Dielectric for GaAs HBT Device, ***Yao-Ting Shao**, C Hua,* WIN Semiconductors Corp., Republic of China

One well known application of ALD method is to deposit a high-k film as a capacitor dielectric. Single film, HfO_2 and Al_2O_3, as MIM capacitor deposited at 300C with 600A of thickness was evaluated first. 900A of PECVD Si_3N_4 film was deposited at 300C for comparison. The capacitance density and breakdown field are listed in table 1. The capacitance density of HfO_2 was high as expected, but breakdown field was too low to pass Time Dependent Dielectric Breakdown (TDDB) lifetime of 20 years at 20V that is a typical reliability requirement for the GaAs HBT device.

In order to pass the TDDB requirement four different laminate structures as capacitor dielectrics were designed with HfO_2 and SiO_2 deposited by ALD at 300C. The film thickness of HfO_2 (630Å) and SiO_2 (144Å) were fixed for the four different structures listed in table 2. HfO_2 are the first and last layers of those structures to ensure that the interface effect between dielectric and metal will be the same. Theoretically, the capacitors of four different dielectric structures should have the same capacitance density. But figure 1 shows that they exhibited significantly different capacitance densities and breakdown voltages at room temperature.

TDDB lifetime was tested afterwards shown in Figure 2. Extrapolation was applied to calculate lifetime at 20V after higher voltage stress at 125C. We found that L17 capacitor at 20 volts had the shortest lifetime than that of sample L9 and L3 capacitors. However,the breakdown voltage of L17 at room temperature was the highest. These reliability results were unexpected. The capacitance behavior of L3 and L17 at high temperature was investigated as well. The capacitance of L17 increased ~1.6% higher than that of L3, ~1.1% increase as temperature changed from 25°C to 150°C.

The capacitance density of L3 is a bit lower, but it exhibits high TDDB lifetime and less capacitance variation as the temperature is increased. This indicates that simple laminate L3 is much more attractive than complicated laminate L17 for GaAs HBT device. More related data will be presented in the conference.

EM-MoP-18 Atomic Layer Deposition of Mo-doped VO_2 Thin Films by Nanolamination of VO_2/MoO_3 Alternating Layers, ***Xinrui Lv**, Y Yu, Y Cao,* Chinese Academy of Sciences, China

Mo-doped VO_2 thin films were fabricated by nanolaminated packing of VO_2/MoO_3 alternating layers using atomic layer deposition (ALD). In the deposition process, tetrakis-dimethyl-amino vanadium (IV) (TDMAV) and molybdenum hexacarbonyl [$Mo(CO)_6$] were used as vanadium precursor and molybdenum precursor, respectively. The deposition temperature was studied to satisfy the requirement of ALD temperature window for both metal precursors, which was testified as around 165 °C. Studies showed that the doping concentration of Mo in VO_2 depends on the ratio of ALD cycle number of molybdenum precursor to that of vanadium precursor. Additionally, effect of doping concentration on the semiconductor-to-metal transition (SMT) characters of VO_2 was also studied, and a considerable reduction of phase transition temperature (T_c) was observed in Mo-doped VO_2 thin films.

EM-MoP-19 Trace Metal Analysis on SiC Wafers using ICP-MS, ***Jaya Chowdhury**,* ChemTrace

High level power electronic devices such as SiC-MOS, SiC SiC-IGBT's are used in power electronic devices. High purity semi-insulating Silicon carbide (HPSI-SiC) wafers are widely used as the substrate replacing silicon in this case. Naturally, the defect free SiC substrate is necessary for a stable and high performing product. Understanding surface metal contamination distribution on SiC wafers is becoming a necessity with the use of these substrates in MOSFET's.

In this paper we will demonstrate a technique that has been developed for revealing high levels of trace metal impurities with high accuracy and sensitivity on the surface of the silicon carbide wafer materials. We will present data from several batches to validate necessity of quantifying the presence of high levels of TM contaminant present in un-acceptable amounts.

EM-MoP-23 Atomic Layer Deposited Single Crystal High-k Y-doped Cubic HfO_2 on GaAs(001) Utilizing HfO_2/Y_2O_3 Super-cycles, ***Lawrence Boyu Young**, C Cheng, Y Lin, K Lin,* National Taiwan University, Republic of China; *C Hsu,* National Synchrotron Radiation Research Center, Republic of China; *J Kwo,* National Tsing Hua University, Republic of China; *M Hong,* National Taiwan University, Republic of China

Si-based complementary metal-oxide-semiconductor (CMOS) technology has reached its physical limit as the scaling-down process is no longer available since the 22-16 nm node. To overcome this challenge, diverse solutions have been proposed in the past few decades. One of the most promising solutions is to replace the Si channel and SiO_2 gate dielectrics by high mobility III-V compound semiconductor and high-k gate dielectrics. Among the III-V compound semiconductors, GaAs with (001) orientation is a promising candidate to be integrated with the conventional Si(001) platform because of the relatively smaller lattice mismatch to Si than those of most of other III-V semiconductors. As the CMOS technology keeps scaling down in its dimensions, we urgently need materials with higher dielectric constant > 30 to push sub 7-nm CMOS technology. There are three well-known phases for HfO_2, monoclinic, cubic, and tetragonal phase, with the dielectric constants of 20, 30, and 70 (by calculation); the cubic and tetragonal phases are unstable at room temperature. In our previous work, we have successfully grown single crystal cubic HfO_2 on GaAs(001) by using MBE through 19% Y-doping1. In order to explore the potential of cubic HfO_2, it is necessary to demonstrate single crystal growth of cubic HfO_2 by utilizing ALD. In this work, we have epitaxially grown single-crystal cubic Y-doped HfO_2 (YDH) on GaAs(001) substrate using ALD HfO_2/Y_2O_3 super-cycles. The reflection high energy electron diffraction (RHEED) patterns revealed that the surface of the deposited YDH exhibited four-fold symmetry (Fig. 1). We have performed synchrotron radiation x-ray diffraction (SR-XRD) study to further study the crystal structure of the films. From the radial scan along the substrate normal, the two strong and sharp peaks located at 31.618^o and 66.043^o are attributed from the substrate GaAs(002) and GaAs(004). The only other two peaks observed at 34.88^o and 73.66^o are corresponding to the d-spacing of 0.257 nm and 0.128 nm, from which a lattice constant of 0.5136 nm was calculated, which is close to our previous result of MBE grown single crystal YDH. The off-normal ϕ-cone scan across the YDH{111} was performed to confirm the symmetry of the structure. The peaks were spaced by a 90° equal spacing, indicating that the structure exhibits a four-fold symmetry (Fig. 2). Furthermore, from the positions of GaAs{111} and YDH{111}, we have determined the epitaxial relationship between YDH and GaAs to be YDH(001)[010]//GaAs(001)[010].

#LBY, CKC, and YHL have contributed equally to this work.

*CHH, JK, and MH are the corresponding authors.

1Z. K. Yang et al, Appl. Phys. Lett. 90, 152908 (2007)

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Cao, Y: EM-MoP-18, 8
Caruso, A: EM-MoP-13, 7
Celebioglu, A: EM+AA-MoA-15, 3
Chen, C: EM+AA-MoA-8, 2
Cheng, C: EM-MoP-23, 8
Cheng, L: EM-MoP-14, **7**
Chitturi, V: EM-MoP-3, 5; EM-MoP-5, **5**
Choi, C: EM-MoP-3, 5; EM-MoP-5, 5
Choi, S: EM-MoP-9, 6
Chowdhury, J: EM-MoP-19, **8**
Christensen, S: EM+AA-MoA-11, **2**
Chung, W: EM-MoP-4, 5
Closser, R: EM+AA-MoA-5, 1
Cobb, P: EM-MoP-3, 5
Colombo, L: EM-MoP-14, 7
Currie, M: EM-MoP-16, 7
— D —
Detavernier, C: EM-MoP-8, 6
Devi, A: EM+AA-MoA-3, 1
Dhara, A: EM-MoP-11, **6**
Dokania, A: EM+AA-MoA-14, 3
Dorsett, L: EM-MoP-13, 7
Downey, B: EM-MoP-16, 7
Drake, A: EM+AA-MoA-12, 3
Dusoe, K: EM+AA-MoA-6, 2
— E —
Eddy, Jr., C: EM-MoP-16, 7
Elias, M: EM-MoP-10, **6**
Eren, H: EM+AA-MoA-15, 3
— G —
Giedraityte, Z: EM+AA-MoA-3, 1
Goulas, A: EM+AA-MoA-14, 3
Griffin, M: EM+AA-MoA-11, 2
Grillo, F: EM+AA-MoA-14, 3
Gungor, N: EM-MoP-15, 7
— H —
Hall, R: EM+AA-MoA-12, 3
Hellstern, T: EM+AA-MoA-5, 1
Hens, Z: EM-MoP-8, 6
Hoglund, J: EM-MoP-12, 6
Homola, T: EM-MoP-1, 5
Hong, M: EM-MoP-23, 8
Horrell, A: EM+AA-MoA-12, 3
Hsu, C: EM-MoP-23, 8
Hua, C: EM-MoP-17, 8
Hurst, K: EM+AA-MoA-11, 2
Hwang, B: EM-MoP-4, 5
— J —
Jeong, H: EM-MoP-3, 5; EM-MoP-5, 5
Ju, L: EM-MoP-6, **5**
Jungjohann, K: EM-MoP-16, 7
— K —
Karppinen, M: EM+AA-MoA-1, **1**; EM+AA-MoA-3, 1
Kedronova, E: EM-MoP-10, 6
Ketola, B: EM-MoP-4, 5
Kim, D: EM+AA-MoA-13, **3**
Kim, H: EM+AA-MoA-13, 3; EM-MoP-7, **5**
Kim, J: EM-MoP-14, 7
Kim, M: EM-MoP-14, 7
King, S: EM-MoP-13, 7
Kisslinger, K: EM+AA-MoA-6, 2
Knez, M: EM+AA-MoA-8, **2**
Kodas, M: EM+AA-MoA-12, 3
Korolev, A: EM-MoP-3, 5; EM-MoP-5, 5
Kozen, A: EM-MoP-16, **7**
Krumpolec, R: EM-MoP-1, 5
Kuhs, J: EM-MoP-8, **6**
Kwo, J: EM-MoP-23, 8
— L —
Lee, C: EM-MoP-4, 5
Lee, J: EM-MoP-14, 7
Lee, S: EM+AA-MoA-6, 2; EM-MoP-9, **6**
Leng, C: EM+AA-MoA-7, 2
Liang, X: EM+AA-MoA-16, 3
Lillethorup, M: EM+AA-MoA-4, 1
Lin, K: EM-MoP-23, 8
Lin, Y: EM-MoP-23, 8
Lingam, H: EM-MoP-3, **5**; EM-MoP-5, 5
Losego, M: EM+AA-MoA-7, **2**
Lucero, A: EM-MoP-14, 7
Lv, X: EM-MoP-18, **8**
— M —
Macák, J: EM-MoP-1, 5
MacIsaac, C: EM+AA-MoA-4, 1; EM+AA-MoA-5, **1**
Mai, L: EM+AA-MoA-3, **1**
Makai, L: EM-MoP-12, 6
Malik, S: EM-MoP-13, 7
Maydannik, P: EM-MoP-1, 5
McBee, J: EM-MoP-12, 6
Millward, A: EM-MoP-4, 5
Moulijn, J: EM+AA-MoA-14, 3
Mun, K: EM-MoP-7, 5
Musgrave, C: EM+AA-MoA-12, 3
— N —
Nam, C: EM+AA-MoA-6, **2**
Natarajan, G: EM-MoP-1, 5
Necas, D: EM-MoP-10, 6
Nielsch, K: EM-MoP-2, 5
Nim, M: EM-MoP-7, 5
— O —
Ondracka, P: EM-MoP-10, 6
O'Toole, R: EM+AA-MoA-12, 3
— P —
Paquette, M: EM-MoP-13, **7**
Park, J: EM+AA-MoA-13, 3; EM-MoP-7, 5; EM-MoP-9, 6
Přikryl, J: EM-MoP-1, 5
— Q —
Qin, Y: EM+AA-MoA-8, 2
— R —
Ranjith, K: EM+AA-MoA-15, 3
Ravichandran, A: EM-MoP-14, 7
Rekken, B: EM-MoP-4, 5
Rogalla, D: EM+AA-MoA-3, 1
— S —
Saha, D: EM-MoP-11, 6
Sarkar, S: EM-MoP-11, 6
Schmidt, M: EM+AA-MoA-3, 1
Schneider, J: EM+AA-MoA-5, 1
Scholz, S: EM+AA-MoA-3, 1
Shamamian, V: EM-MoP-4, 5
Shang, Z: EM+AA-MoA-16, **3**
Shao, Y: EM-MoP-17, **8**
Stein, A: EM+AA-MoA-6, 2
Strandwitz, N: EM-MoP-6, 5
Strickler, A: EM+AA-MoA-4, 1
Suh, D: EM-MoP-3, 5; EM-MoP-5, 5
Sundaram, G: EM-MoP-12, 6
Sunderland, T: EM-MoP-4, 5
— T —
Telgenhoff, M: EM-MoP-4, 5
Thomas, A: EM-MoP-2, 5
Tynell, T: EM-MoP-2, **5**
— U —
Uyar, T: EM+AA-MoA-15, **3**
— V —
Valdesueiro, D: EM+AA-MoA-14, 3
Van Bui, H: EM+AA-MoA-14, 3
van Limpt, B: EM+AA-MoA-14, **3**
van Ommen, J: EM+AA-MoA-14, 3
Vardon, D: EM+AA-MoA-11, 2
Vida, J: EM-MoP-10, 6
— W —
Wallace, R: EM-MoP-14, 7
Wang, Q: EM-MoP-14, 7
Wang, W: EM+AA-MoA-8, 2
Wang, X: EM-MoP-4, 5
Weimer, A: EM+AA-MoA-12, 3
Wheeler, V: EM-MoP-16, 7
Wieck, A: EM+AA-MoA-3, 1
Wiegand, C: EM-MoP-2, 5
— Y —
Yang, F: EM+AA-MoA-8, 2
Yang, N: EM+AA-MoA-4, 1
Ye, X: EM+AA-MoA-6, 2
Young, L: EM-MoP-23, **8**
Yu, Y: EM-MoP-18, 8
— Z —
Zajickova, L: EM-MoP-10, 6
Zazpe, R: EM-MoP-1, 5
Zhou, X: EM-MoP-4, **5**
Zhu, H: EM-MoP-14, 7