Hybrid Materials & Infiltration
Room Arteveldeforum & Pedro de Gante - Session HM+EM+NS-MoP
Hybrid Materials & Infiltration Poster Session

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

Sequential infiltration synthesis (SIS) has emerged in the past decade as a powerful technique for growth of inorganic materials within polymers through ALD chemistry. In SIS, ALD precursors diffuse into the polymer and interact with it, leading to inorganic materials growth within the polymer's free volume. If desired, the polymer can later be removed, yielding polymer-templated inorganic structures.

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

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

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

In our work, we use first principles density functional theory calculations to examine key steps in the mechanism of hybrid film deposition through MLD by modelling precursor-surface and precursor-precursor reactions and challenging the proposed reaction mechanisms in hybrid films. We explore the growth mechanism of aluminium, magnesium and titanium containing hybrid films known as alucones, magnesicones and titanicones, respectively. For alucones we investigate in detail the chemistry of the MLD process between the post-TMA (Al(CH$_3$)$_3$) pulse methyl-terminated Al_2O_3 surface with ethylene glycol (EG) and glycerol (GL). Double reactions of organic molecules with the alumina surface are also explored. We show that while both organic precursors react favorably with TMA fragments, EG and GL lie flat and create double reactions through the two terminal OH groups. For EG this phenomenon removes the active OH groups from the surface and growth will be less favorable while for GL the third OH group is available and growth can proceed. [1] Because of the double reaction phenomenon of aliphatic molecules EG and GL, we proposed new aromatic molecules which due to their stiff backbone avoid the unwanted double reactions and lead to thicker and more flexible hybrid films.[2] As the infiltration phenomenon of TMA into the growing film is another common practical issue in alucone film growth, we consider DMAI ((CH$_3$)$_2$Al(OC$_3$H$_7$))as an alternative to TMA. DFT calculations show that the reactivity of DMAI is sufficient for DMAI to take part in the MLD reactions. Combined with the fact that DMAI is a bulky molecule that avoids infiltration into the alucone film, DFT studies provide motivation to develop an MLD process using DMAI as inorganic precursor.

We also investigate the growth mechanism of titanicones grown using TiCl$_4$ and TDMATas metal source and EG or GL as organic reactants. We found that compared to TiCl$_4$, TDMAT adsorbs more favorably on the anatase-TiO$_2$, rutile-TiO$_2$ and Al_2O_3 surfaces and reacts more favorably with the organic species. Therefore, TDMAT is a more suitable precursor for titanicone film growth.

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HM+EM+NS-MoP-3 Hybrid Organic-Inorganic Isoporous Membranes with Tunable Pore Sizes and Functionalities for Molecular Separation, *Z. Zhang,* Helmholtz-Zentrum hereon GmbH, Germany; *Assaf Simon, T. Segal-Peretz,* Technion IIT, Israel*; V. Abetz,* Helmholtz-Zentrum hereon GmbH, Germany

Block copolymers (BCPs) are considered promising materials for various membrane applications ranging from water treatment to protein separation due to their ability to self-assemble into highly ordered structures with uniform pore size and high pore density. Typically, the pore's size and surface interactions are controlled by the BCP chemistry. However, simultaneous control over both properties is difficult to achieve. In particular, reaching nanometric pores which will allow for molecular separation through the BCP chemistry is considered a major challenge.

In this study, we tailor the size and chemistry of BCP based ultrafiltration membranes by selectively growing metal oxides within and on the pores. Poly (styrene-*b*-4-vinyl pyridine) (PS-*b*-P4VP) was used to create ultrafiltration membranes in a process combining self-assembly with non-solvent induced phase separation (SNIPS). This results in one integral but asymmetric membrane, with ordered pores at the top of the membrane and sponge-like mechanically robust support layer at the bottom of the membrane. Sequential infiltration synthesis (SIS), an atomic layer deposition-based technique that enables selective growth of metal oxides inside the polar domains of BCP, was used to grow Al_2O_3 inside the P4VP domains of the BCP films. By incorporating metal oxides in the pores, the pore size can be reduced. By modifying the number of SIS cycles and/or the metal oxide we use, we can achieve control over the pore size while laying grounds for further membrane functionalization.

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

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

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

The removal of excess CO_2 from the atmosphere will play a major role in the mitigation of global warming. While CO_2 sequestration at fossil fuel power plants is primarily achieved via wet chemical routes, CO_2 capture from ambient air is much more challenging. Solid-state adsorbents, consisting of CO_2-binding functional amine groups on porous supports, can deliver high CO_2 capture capacities with low energy requirements[1].

In this contribution, we report on the functionalization of porous carbon fibers by self-limiting vapor-phase techniques. Functionalization was carried out either via i) exposure to a cyclic azasilane molecule (2,2-dimethoxy-1,6-diaza-2-silacyclooctane) to introduce amine functionalities or ii) ALD of Al_2O_3 based on cycles of trimethylaluminum and H_2O followed by exposure to the azasilane molecule. Given the high specific surface area of the carbon fibers exceeding 1400 m^2/g with a bimodal distribution of pore diameter (0.5-0.6 nm and 0.8 nm), the above-mentioned precursors were dosed in multi-pulses.

The self-limiting nature of the two processes was verified by weight gain measurements. The increase in weight relative to the pristine sample saturated at 23% for direct amine functionalization. For case ii), the weight gain saturated at 11% for Al_2O_3 ALD and at 3.1% upon azasilane exposure relative to the pristine sample. The lower amine loading in case ii) with respect to case i), i.e. 0.14 mmol/g vs. 0.97 mmol/g, respectively, may result from clogging of smaller pores by ALD of Al_2O_3. XPS analysis confirmed amine functionalization, while EDX mapping of fiber cross-section revealed an homogenous distribution of Al and Si.

CO_2 capture capacities of 0.18 and 0.13 mmol/g$_{sorbent}$ were measured under simulated ambient conditions by mass spectrometry for case i) and ii),

respectively. The capture capacities were in the same range as those reported for amines grafted on SiO_2[2,3]. However, the capture capacity with respect to amine loading for case ii) was 5-fold exceeding case i). This indicates that the functionalization of carbon fibers by ALD of Al_2O_3 and azasilane exposure leads to an efficient utilization of amine groups for CO_2 capture.

The presented research demonstrates the potential of modifying porous carbon fibers by grafting CO_2 adsorption functionalities via vapor-phase methods on the fibers' internal surface. Future engineering of porous materials by ALD and vapor-phase functionalization may pave the way towards realizing efficient direct air capture.

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HM+EM+NS-MoP-5 Mechanical Behavior of Hybrid Organic-Inorganic Thin Films Fabricated by Sequential Infiltration Synthesis (SIS), *Shachar Keren, T. Segal-Peretz , N. Cohen,* Technion, Israel
Hybrid organic-inorganic materials have drawn increased interest in the last decades due to their synergic properties. Control over the mechanical properties of hybrid organic-inorganic nanomaterials is central to their implementation in a wide range of applications, including energy absorbing materials and protective coatings. In recent years, sequential infiltration synthesis (SIS) has emerged as a promising new technique for fabricating hybrid materials with nanoscale precision. In SIS, inorganic materials are grown within polymers from vapor phase precursors using atomic layer deposition (ALD) chemistry. Several studies have demonstrated the potential of SIS to tune the mechanical properties of polymers. However, a full understanding of the relationship between the nanoscale structure and composition and the nanostructure mechanical behavior is still an ongoing effort.

In this research, we study the mechanical response of pristine and hybrid thin films fabricated via SIS using a combined experimental and theoretical approach. Hybrid thin films were fabricated by growing AlO_x within PMMA films via SIS process, using trimethylaluminum and H_2O as precursors. *In-situ* FTIR measurements were used to evaluate the interaction between the inorganic AlO_x and the polymer chains, and *in-situ* microgravimetric measurements were used to assess the inorganic mass gain. The mechanical responses were studied with nanoindentation combined with scanning electron microscopy (SEM). In addition, we developed a microscopic model which accounts for the hybrid organic-inorganic microstructure profile and correlates between the hybrid structures and their mechanical properties.

HM+EM+NS-MoP-6 Plasma Enhanced-MLD Processes of Phosphorus-Containing Thin Films, *Justin Lomax,* University of Western Ontario, Canada*; E. Goodwin, P. Gordon,* Carleton University, Canada*; C. McGuiness,* Solvay, Canada*; S. Barry,* Carleton University, Canada*; C. Crudden,* Queen's University, Canada*; P. Ragogna,* University of Western Ontario, Canada
Since the introduction of Molecular Layer Deposition (MLD), many compounds have been employed as a precursor to generate thin films of materials on the angstrom scale. Examples include amides, ureas, thioureas, azomethines, ethylene terephthalates, and ester precursors for thin film construction.[1] MLD films have been prepared with relatively few elements other than C, N, O, and S, leaving vast areas on the periodic table open for investigation. The Ragogna group has developed a method of preparing robust phosphorus polymer networks that in the bulk phase show excellent surface adhesion, barrier properties (O_2; H_2O), optical transparency (visible) and thermal stability (up to 400 °C).[2] This known method of generating polymer networks rich in phosphorus content was translated into an MLD process. By using plasma-enhanced MLD on Si/SiO_2 and Al_2O_3 substrates, film generation using the commercially available 1° phosphine *i*BuPH$_2$ paired with a known volatile siloxane precursor (tetramethyltetravinylcyclotetrasiloxane) was explored. Thin film construction (10-100 nm) used an Ar radical source to facilitate P-H addition to the vinyl functionalities on the siloxane precursor and yielded a growth rate of 0.6 - 1.45 Å per cycle. Films were characterized by XPS, AFM and ToF-SIMS.

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HM+EM+NS-MoP-7 Al_2O_3 Dot and Antidot Arrays Fabricated by Sequential Infiltration Synthesis in Hexagonally Packed PS-*b*-PMMA Block Copolymer Thin Films, *Gabriele Seguini, A. Motta, M. Bigatti, F. Caligiore,* CNR, Italy*; G. Rademaker, A. Gharbi, R. Tiron,* CEA/LETI-University Grenoble Alpes, France*; G. Tallarida, E. Cianci, M. Perego,* CNR, Italy
Sequential infiltration synthesis (SIS) is a three-dimensional (3D) growth process derived from atomic layer deposition (ALD) on polymers. SIS permits to grow inorganic materials into polymeric films. SIS into self-assembled block copolymers (BCP) offers the possibility to fabricate inorganic nanostructures starting from nanostructured organic templates. The fine-tuning of the dimensions of the resulting nanostructures can be achieved by proper selection of the SIS process conditions. In particular, the sequential reaction steps of the SIS process allow tuning the dimensions of the nanostructured material adjusting the number of SIS cycles. This capability to achieve a fine tuning of the dimensions of the resulting inorganic nanostructures is fundamental to make this technology suitable for the different target applications. At the same time, this step by step growth of the inorganic nanostructures allows to obtain information about the progressive mass uptake of the inorganic component into the polymer matrix and to delve into the growth mechanism.

In this work, Al_2O_3 dot and antidot arrays were synthetized by infiltration of trimethylaluminum and water precursors into out of plane cylinder forming poly(styrene-block-methyl methacrylate) (PS-b-PMMA) BCP thin films. The evolution of the characteristic dimensions of these inorganic nanostructures were investigated as a function of the SIS cycle number. Collected data provided information about the mechanism governing the effective incorporation of Al_2O_3 into the PMMA component of the BCP thin films. Accordingly, mass uptake of Al_2O_3 into the PMMA component of self-assembled PS-b-PMMA thin film is significantly enhanced compared to mass uptake in pure PMMA thin films, due to the presence of additional paths for diffusion of precursor molecules into the not reactive PS component and to their sorption at the PS/PMMA interface. Mass uptake is directly proportional to the surface of the PMMA nanodomains suggesting that in this specific BCP system the incorporation of Al_2O_3 into the PMMA component is essentially sorption limited. From the technological point of view, collected data demonstrate that SIS provides accurate control on the characteristic dimensions of the Al_2O_3 dot and antidot arrays.

HM+EM+NS-MoP-8 Flexible and Conductive Zinc oxide – Zincone Nanolaminate Thin Films Deposited using Atomic and Molecular Layer Depositions, *Seung Hak Song, B. Choi,* Korea University, Korea (Republic of)
The combination of atomic layer deposition (ALD) and molecular layer deposition (MLD) enables the fabrication of various functional organic-inorganic composite thin film structures. By adjusting ALD and MLD cycles ratio, the structure of organic-inorganic thin films can be controlled. Therefore, the properties of the thin films can be tuned through the combination of various nano layers. Flexibility can be improved by inserting organic layers between thicker inorganic thin films. Incorporation of organic layers may degrade the electrical properties of thin films due to decrease in crystallinity. Therefore, it is necessary to study the thin film structures with optimal mechanical and electrical properties. Although the combination of ALD and MLD is very promising, few studies have been conducted. Especially, there are very few studies on the mechanical properties of organic-inorganic nanolaminate thin films, and studies have been conducted on very limited areas. We deposited zinc oxide (ZnO) – zincone nanolaminate thin films on transparent polyimide (TPI) using ALD and MLD methods and investigated their growth characteristics and mechanical-electrical properties with process conditions. We fabricated thin films with ZnO and zincone ratios of 100:1, 40:1 and 20:1 respectively, in the temperature range of 120 to 240 ℃ and measured the changes in mechanical-electrical properties according to deposition temperature and thin film structures. The mechanical properties of the thin films were measured through nanoindentation and bending tests. The bending test is a method to evaluate the durability of the thin films by measuring the change in electrical resistance of the thin films with bending radius, and it was possible to analyze the effect of zincone layers on the thin film's durability. In addition, changes in the microstructures of the thin films with process temperature were measured using X-ray diffraction (XRD) and

transmission electron microscopy (TEM), and the effect of microstructural changes on mechanical and electrical properties of the thin films were analyzed. From the tests results, as the zincone ratio increased, the crystallinity of the thin films decreased and the electrical conductivity was lowered, but the flexibility was slightly improved.

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

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

In this work, we investigated the growth of Al_2O_3 in freestanding ~30 um thick PBS films by SIS process at 70°C via trimethylaluminum (TMA) and H_2O precursors. Through a systematic analysis of the composition and morphology of the infiltrated PBS samples at different process conditions, the reaction kinetics was clarified. FTIR and NMR measurements showed that the ester group is involved in polymer-precursors interaction, leading to the formation of a new aliphatic groups with the concomitant rupture of the main polymeric chain. Al_2O_3 incorporation in the infiltrated samples was further confirmed by the XPS analysis. Moreover, SEM-EDX cross sectional images showed a homogeneous Al_2O_3 distribution inside the PBS films, depicting a completely different scenario compared to standard ALD that determines Al_2O_3 growth on the more superficial region of the PBS film. Al_2O_3 mass uptake as a function of the number of SIS cycles was studied by infiltration in thin PBS films spin coated on Si substrates ranging from 30 to 70 nm. Mass uptake in the PBS films was found to be much higher than in standard polymethylmethacrylate films, at the same process conditions. Considering that the density of reactive sites in the two polymers is roughly the same, the observed difference in Al_2O_3 mass uptake is explained based on the different free volume of these polymers and the specific reaction mechanism proposed for PBS. These results pave the way towards the application of SIS for the improvement of bio-polymers for food packaging.

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

Sequential infiltration synthesis (SIS), an ALD-derived method for growth of inorganic materials inside polymeric structures, is an emerging technique for hybrid materials and inorganic nanostructure fabrication which can be utilized in a wide array of applications. In this work, we study the development of ZnO crystalline particles within SU-8, polymethacrolein (PMCHO), and polymethyl methacrylate (PMMA) at the atomic scale. We probe the growth throughout diethyl zinc (DEZ)/H_2O SIS cycles, as well as after polymer removal. The crystalline ZnO structure is deciphered by combining two powerful methods: extended x-ray absorption fine structure (EXAFS) and high-resolution scanning transmission electron microscopy (HR-STEM). Synchrotron-based EXAFS provides large-scale statistical information on the crystals' long-range order and predicts their Wurtzite structure. HR-STEM of the hybrid polymer-ZnO films corroborates the predicted structure and allows for precise analysis of crystal size, orientation, and existing defects, as well as the dispersion of the particles inside each polymer. Significantly, the polymer matrix allows us to probe the growth, cycle-by-cycle, providing insights to ZnO atomic growth mechanism inside different polymers and extending our understanding of

SIS. In addition, the methodology developed for such high-resolution imaging of hybrid films will allow future studies of additional hybrid systems.

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

Hafnium dioxide (hafnia, HfO_2) is a transition-metal oxide, an electrical insulator with a large energy bandgap ~5.5 eV. Among numerous applications of this material, its thin films have been used as gate insulators in transistors and as optical and corrosion-protective coatings. The scope of applications for porous hafnia nanostructures is even more extensive and includes catalytical and sensing applications.

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

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

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

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

Among the different gas sensing platforms, cantilever-based sensors have attracted considerable interest in recent years thanks to their ultra-sensitivity and high-speed response. The gas sensing mechanism in a dynamic cantilever sensor is based on its resonance frequency shift upon adsorption of a gas molecule on the sensor. In order to sensitize the surface of a cantilever, a sensitive receptor material with large surface area is required. Metal-organic frameworks (MOFs) are a class of nanoporous crystalline materials composed of metal ions coordinated to organic linkers. MOFs are promising for gas sensing applications as they have large surface area, rich porosity with adjustable pore size and excellent selective adsorption capability for various gasses.[1] Zeolite imidazole frameworks (ZIFs) are a class of MOFs where metals with tetrahedral coordination (i.e. Zn, Co, Fe, Cu) are the central node and the ligands are imidazolate-based organic   molecules.

In this work, we developed a ZIF-based thin film for dynamic cantilever gas-sensing applications. We employed a novel atmospheric pressure spatial atomic layer deposition (AP-SALD)[2][3] technique to deposit a ZnO sacrificial layer on the silicon cantilevers. This technique allows the deposition of high-quality films at atmospheric pressure, faster than conventional ALD. The ZnO layer was then converted to a particular ZIF film with desired porosity and size, through a MOF-CVD process.[4] A gas-

sensing bench setup was developed for the cantilever actuation and read-out. We present the chemical and morphological properties of the ZIF, as well as the frequency response of the sensor to various gases. The device showed reliable sensitivity to humidity, CO2 and several VOCs.

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

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

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

In recent years, research on monolayer and two-dimensional (2D)-based family materials developed, starting with well-known graphene which has emerged an innovative research topic[1]. Through atomic-level thickness control of ultra-thin 2D materials, the design and fusion of electronic devices are possible, enabling applications in various fields as well as in optoelectronics and semiconductors. Organic/inorganic hybrid tincone films were deposited by molecular layer deposition (MLD) using N,N'-tert-butyl-1,1-dimethylethylenediamine stannylene(II) as a precursor and hydroquinone (HQ) as organic reactants. When combined with HQ having a bi-functional hydroxyl group, SnO-based 2D hybrid tincone can be produced. In this study of tincone fabricated with a divalent precursor after a vacuum post-annealing process, the structural rearrangement of the SnO and the benzene ring bonds proceeded to form a SnO-based hybrid 2D structure. The rearrangement of the resulting structure occurred through π-π stacking (without pyrolysis) of the benzene ring. To understand the mechanism of fabrication of 2D hybrid tincone by π-π stacking of the benzene ring, and the strengthening of the crystallinity of SnO after the annealing process, the structural rearrangement was observed using X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffraction (GIXRD), grazing-incidence wide-angle X-ray scattering (GIWAXS), and Raman spectra.

As seen in the analyses, the as-deposited tincone originally had weak SnO nano-crystallinity without a specific crystal orientation. One hour after the annealing process at 400 ℃, individual benzene ring bonds were combined with the SnO layer in a repeated arrangement of tincone monomer [-Sn-O-C$_6$H$_4$-O-]n. In the visible region (380–750 nm), high transparency (>85%) enabled optical device application through a hybrid layer with the SnO.

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

Nowadays innovation in food packaging is considered at the edge of studies to extend the shelf life of food packaging, and prevent microbial spoilage, chemical contaminants, moistures, etc. In order to confer such properties into these materials one of the very promising strategies is to use molecular layer deposition (MLD). In this work, the growth of thin films via MLD are obtained by using malonyl chloride (MC) and 1.6-hexanediamine (HD) as a precursor resulting in the in-situ synthesis of the compound designated as Nylon 6,4.

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

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

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

Nanostructure Synthesis and Fabrication
Room Arteveldeforum & Pedro de Gante - Session NS-MoP
Nanostructures Synthesis and Fabrication Poster Session

NS-MoP-1 Atmospheric Pressure ALD to Increase Organic Solvent Resistance of PDMS, *Albert Santoso, A. Damen, S. Khedoe, V. van Steijn, R. van Ommen,* Delft University of Technology, Netherlands

In the field of microfluidics, PDMS (polydimethoxysilane) is one among the most used polymers since it is cheap and allows easy device fabrication. On top of its high transparency, PDMS is also known to be amiable with cells and harsh inorganic solvents, making it good candidates for fluidic researches. However, there is one big downside of PDMS, which is its incompatibility with organic solvents. As a result, swelling of the polymer, and subsequently microchannel collapse, render the use of PDMS microfluidics in oil-water system such as emulsion and liquid-liquid extraction. Furthermore, current researches in increasing the so-called organic solvent "barrier resistance" are limited to finding alternative materials, which ignores the whole benefit of PDMS bulk properties. Therefore, there is a need to increase PDMS' barrier resistance without changing the bulk property. We investigate surface modification using atomic layer deposition (ALD) as an approach to improve the barrier properties of PDMS. Metal oxide such as 'bio-friendly' titanium oxide can be deposited with atomic level precision, leading to formation of barrier layer without compromising other properties of PDMS. This study focuses on the use of atmospheric pressure atomic layer deposition (APALD) on flat thin film PDMS. Compared with the conventional vacuum ALD, the convective transport allows gaseous ALD reactant to flow in high aspect ratio microfluidic channel, which is a big potential in in-situ deposition. The result shows that PDMS film coated with APALD layer has an equilibrium mass swelling ratio of 1.06 after exposure with cyclohexane. This is a large improvement than the non-coated PDMS (1.25) and the ones coated with vacuum ALD (1.22). Further investigation using scanning electron microscopy shows that uniform coating is important to reduce the organic solvent intake. Furthermore, the formation of mixed layer due to ALD reactant infiltration in the PDMS during APALD contributes in the formation of robust and crack-free surfaces, as shown by x-ray photoelectron

spectroscopy depth profiling. As an addition, little to no changes are observed in the transparency and mechanical property of PDMS. This study opens up potential of in-situ coating of PDMS microfluidic, that can be used in the field of bio-radio-assays, emulsion, and extraction with organic solvent.

NS-MoP-2 The Fabrication of Heterojunctions by Atomic Layer Deposition for Gas Sensing Application, *Muhammad Hamid Raza*, *N. Pinna*, Humboldt-Universität zu Berlin, Germany

Material and methods for detecting a wide range of harmful species are becoming increasingly necessary as automation and industrial growth increase. Chemoresistive gas sensors using semiconducting metal oxides (SMOX) are fundamental for developing efficient gas sensors. The sensitivity and selectivity of these nanostructured SMOX can be boosted by combining them with other SMOX. Yet control over the thickness of the shell layer is crucial; particularly, a thin shell layer modulates the space charge layer at the interface, thereby influencing effectively the charge conduction channel. The engineering of heterojunctions with well-defined core and shell layers is required to better understand the sensing response of heterostructured nanomaterials. A comprehensive understanding of the role of semiconductor heterojunctions and the sensing response of core-shell heterostructures is achieved by synthesizing a series of well-defined and well-controlled heterostructures with varying core and shell layers. NiO- and SnO_2-based hierarchical coaxial core-shell heterostructures are therefore proposed to achieve this objective. The designed heterostructures exhibit sensing responses related to the NiO or SnO_2-shell layers, or in some cases to the heterojunctions between $_nSMOX$ (SnO_2) and $_pSMOX$ (NiO). A comparison of the sensing response in order to understand the transduction mechanism across the interfaces in ALD grown heterojunctions will be presented.

NS-MoP-4 Combining Initiated Chemical Vapor Deposition and Plasma-Enhanced Atomic Layer Deposition: A Study of Initial Growth and Interface Formation, *Lisanne Demelius*, *K. Unger*, *A. Coclite*, Graz University of Technology, Austria

In recent years, atomic layer deposition (ALD) on polymer substrates has attracted increasing interest due to potential applications in organic electronics and photovoltaics, as well as for the surface functionalization of packaging and biomaterials. However, the inherent porous structure of polymeric substrates often leads to non-ideal ALD processes that result in precursor diffusion and subsurface growth of the deposited material. The use of plasma-enhanced ALD (PE-ALD) is known to enhance nucleation due to the surface-activating effect of plasma and can be expected to significantly reduce subsurface diffusion, enabling the surface-limited deposition of thin conformal coatings. However, plasma can also have detrimental effects on polymeric substrates causing polymer degradation or etching.

In our work, we have investigated the initial growth of piezoelectric ZnO during PE-ALD on different polymer thin films deposited by initiated chemical vapor deposition (iCVD). iCVD is a prominent method to deposit highly uniform thin films of a wide range of (functional) polymers while fully retaining their rich chemistry. ZnO growth was monitored via in-situ spectroscopic ellipsometry (SE) and the resulting thin films were further characterized in terms of crystallinity, interface and surface morphology and elemental composition. To gain a better understanding of how the chemical structure of the polymer influences ZnO thin film formation, polymers exhibiting varying degrees of reactivity with the ALD precursor were studied. Furthermore, the influence of plasma power on growth behavior was investigated.

Our results show that film formation on the iCVD polymers is a consequence of two competing processes: ZnO PE-ALD growth and plasma etching of the polymer substrate. During the initial ALD cycles, polymer etching dominates, resulting in an overall decrease in thickness. At a certain point, ZnO growth takes over and the regime of normal ALD growth behaviour is entered. The strength of etching is proportional to the applied plasma power and depends strongly on the type of polymer. Despite the initial etching, the resulting thin films exhibit sharp interfaces and a quality, in terms of surface roughness, crystallinity and ZnO density, comparable to those of ZnO deposited on silicon.

This study sheds light on the mechanisms governing initial growth during PE-ALD of ZnO on different polymers and illustrates the potential of the combined use of iCVD and PE-ALD as means to achieve highly uniform and smooth multilayer structures that could be applied in a wide range of functional devices including sensing or actuation.

NS-MoP-11 Synthesis of Novel Composite Thin Film Systems With Outstanding Mechanical Properties, *L. Pethö*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *C. Guerra*, Swiss Cluster, Switzerland; *T. Xie*, *T. Edwards*, *J. Michler*, *X. Maeder*, *Ivo Utke*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Nanoscale multilayered thin films consisting of alternating sublayers of dissimilar materials have attracted extensive attention in recent years due to their electrical, thermal and mechanical properties as compared to their single component counterparts and prove to be very promising for engineering applications. The advantage in mechanical properties are mainly attributed to the dense interfaces and interfacial structure among the different materials that form the multilayers.

We have built a hybrid thin film deposition system by combining physical vapor deposition (PVD) and atomic layer deposition (ALD) into a single machine without breaking vacuum. Multilayer composite systems were synthesized that consist of ALD Al_2O_3 sublayers between pure PVD Al structural layers. By using this system, we obtain precise control of the thickness of each ultrathin alumina layer, well below the native surface oxide thickness of pure aluminum.

We show that the ALD alumina sublayers effectively interrupted the grain growth of the ~250 nm thick Al sublayers by enabling precise grain surface control. Native surface oxide formation on the PVD deposited pure Al sublayers was circumvented by keeping the substrate in high vacuum between processing steps.

The pure Al layers are constituted of equiaxed grains with no epitaxial or texture relationship among the neighboring layers. The Al grain boundaries are parallel to the film growth direction and extend the height of each Al sublayer to form a brick-and-mortar type microstructure.

We have furthermore seen that these multilayer coatings have high yield strength compared to bulk pure aluminum. This is explained by the amorphous alumina layers acting as a dislocation sink, absorbing defects. The high tensile strength and good ductile properties of alumina are shown to restrain the deformation of Al layers and reinforce the structure.

Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS-WeM2

2D Materials I

Moderators: Gregory N. Parsons, North Carolina State University, Henrik Pedersen, Linköping University, Sweden

10:45am **NS-WeM2-1 Atomic Layer Deposition of Layered Chalcogenides**, *Suzanne Mohney*, *J. Carter, I. Campbell, A. Agyapong,* Penn State University **INVITED**

Layered chalcogenide materials with van der Waals bonding between layers are fascinating materials. Some are semiconductors with bandgaps suitable for transistors or have been used in atomically thin memory devices, while others are thermoelectrics or topological insulators that are interesting for quantum devices. Antimony(III) telluride has a layered structure with van der Waals bonds between Te atoms in adjacent quintuple layers. We have performed ALD of Sb_2Te_3 using bis(trimethylsilyl)tellurium and antimony(III) ethoxide, which is a pair of previously reported precursors,[1] expanding the set of studied substrates and employing various surface treatments prior to deposition. Growth of a continuous layer is highly dependent on the starting surface through at least the first 500 cycles. Growth on the van der Waals surface of epitaxial monolayers of MoS_2 was difficult, as has been the case for other thermal ALD processes on transition metal dichalcogenides.[2] On SiO_2, we observed incompletely coalesced islands by SEM. Conversely, on amorphous GeTe, single-crystal Bi_2Te_3, or polycrystalline TiN substrates subjected *in situ* to a remote Ar plasma, we grew continuous Sb_2Te_3. On amorphous GeTe and TiN, we measured a pronounced drop in sheet resistance after 500 cycles. X-ray photoelectron spectroscopy confirms the presence of Sb and Te with $3d_{5/2}$ core levels near 527 eV and 572 eV, respectively. Compared to reference spectra, the ratio of intensities matches the expected stoichiometry. Bi_2Te_3 crystals are interesting because they have the same structure as Sb_2Te_3. In our prior study of plasma enhanced ALD on MoS_2, we observed that growth on single-crystal GaN, which has nearly the same lattice parameter in the basal plane, led to much less out-of-plane growth than on other substrates.[3] In reports on ALD of Sb_2Te_3 with the same Te precursor but antimony trichloride instead of antimony(III) ethoxide,[4] or growth of Sb with analogous chloride and alkylsilyl precursors,[5] engineering the hydroxyl groups on the substrate seems to play an important role in promoting in-plane nucleation and rapid coalescence. However, our experiments with bis(triethylsilyl)tellurium and antimony(III) ethoxide did not show an analogous advantage. We will further consider atomic layer epitaxy of van der Waals solids in this presentation. We thank ONR N0014-18-12511 for support and the NSF 2DCC DMR-1539916 for epitaxial substrates.

1. Eom et al., Chem. Mater. 24, 2099, 2012

2. Walter *et al.*, Appl. Surf. Sci. 480, 43, 2019

3. Mughal *et al.*, J. Vac. Sci. Technol. A 37, 010907, 2019

4. Nminibapiel *et al.*, ECS J Solid State Sci Technol 3P95, 2014

5. Mohney *et al.*, ALD2016

11:15am **NS-WeM2-3 2D Alloys of WS_2 and NbS_2 by PEALD**, *Jeff Schulpen, C. Lam,* Eindhoven University of Technology, The Netherlands; *E. Coleman, F. Gity,* Tyndall National Institute, University College Cork, Ireland; *M. Mattinen, M. Verheijen, E. Kessels,* Eindhoven University of Technology, The Netherlands; *R. Duffy,* Tyndall National Institute, University College Cork, Ireland; *A. Bol,* Eindhoven University of Technology, The Netherlands

2D transition metal dichalcogenides (TMDs) have many unique properties such as high electronic mobilities and a large surface-to-volume ratio, making them promising materials for various applications such as nanoelectronics and electrocatalysis. In particular, *alloys* of 2D TMDs hold great potential due to their composition-controlled properties, making them more versatile than pure TMDs. Atomic layer deposition can be used to synthesize thin films of such TMD alloys with sub-monolayer growth control, making this method particularly relevant for the aforementioned applications. In this work we employ plasma-enhanced atomic layer deposition (PEALD) to synthesize alloys of the 2D TMDs NbS_2 and WS_2, i.e. $Nb_xW_{1-x}S_2$ using $W(NtBu)_2(NMe_2)_2$ and $Nb(NtBu)(NEt_2)_3$ as precursors and H_2S plasma as coreactant. We present a thorough characterization of the alloy growth, showing excellent composition control ranging from nanocrystalline WS_2 to amorphous NbS_2 based on ellipsometry, XPS, SEM, Raman spectroscopy and TEM. The morphology of the films depends strongly on the composition, as the alloy films have a significantly enhanced occurrence of out-of-plane oriented crystallites.

The suitability of $Nb_xW_{1-x}S_2$ as a channel material for transistors is evaluated by Hall measurements and FET device characterization. We find that the incorporation of only 10% Nb reduces the resistivity of the WS_2 film by 4 orders of magnitude at a mobility of 0.3 cm^2/Vs. Furthermore, improving the Nb distribution in the film through consecutive precursor dosing (ABC-type cycles) further increases the mobility by a factor of 2.5. At the same time we observe that the formation of out-of-plane oriented crystallites is strongly suppressed when using this process type, which is critical for applications in nano-electronics. Fabrication and characterization of FETs based on the alloy films are currently ongoing. Secondly, we assess the efficacy of the $Nb_xW_{1-x}S_2$ films as electrocatalysts for the hydrogen evolution reaction (HER). The alloys were found to outperform the pure NbS_2 and WS_2 films deposited by PEALD, having lower Tafel slopes and overpotentials. The alloy with a composition x = 0.84 performed best with a Tafel slope of 131 mV/dec and an overpotential of 470 mV.

Our results show that the $Nb_xW_{1-x}S_2$ alloys improve on the electrical and electrocatalytic performance of pure WS_2 and NbS_2. Furthermore, the various supercycle schemes provide a valuable platform for fundamental insight into the surface reactions and growth mechanics during the PEALD process and for further fine-tuning of the alloy functionalities.

11:30am **NS-WeM2-4 2D Molybdenum Dichalcogenides by Atomic Layer Deposition**, *Raul Zazpe, J. Charvot, L. Hromadko, H. Sopha, J. Rodriguez Pereira , F. Bures, J. Macak,* University of Pardubice, Czechia

2D semiconductor transition metal dichalcogenides have attracted considerable attention due to their layered structure, suitable band gap, electrochemically active unsaturated edges and relatively good stability against photocorrosion. These properties result promising for different applications including, Li-ion batteries, photocatalysis and hydrogen evolution reaction (HER). Apart from the widely studied 2D MoS_2, 2D selenide and telluride equivalents, $MoSe_2$ and $MoTe_2$, have recently gained considerable interest due to their higher electrical conductivity, wider inter-layer distance and narrower bandgap as compared to MoS_2, high surface area and close to zero Gibbs free energy edges for hydrogen adsorption.

Unlike sulfide dichalcogenides, the lack of Se and Te precursors have prevented the synthesis of selenide and telluride dichalcogenides by ALD. In order to surpass such impediment, we present a set of novel in-house synthesized Se and Te compounds, which were successfully combined with commercial Mo precursor to synthesize $MoSe_2$ and $MoTe_2$ by ALD [1-5]. The as-deposited ALD $MoSe_2$ and $MoTe_2$ on substrates of different nature were extensively characterized by different techniques, which confirmed the chemical composition and revealed the growth of 2D flaky nano-crystalline $MoSe_2$ and $MoTe_2$. In parallel, $MoSe_2$ and $MoTe_2$@TiO_2 nanotube layers (TNTs) heterostructures were fabricated in a simple and fast fashion to explore and exploit the $MoSe_2$ and $MoTe_2$ photo- and electrocatalytic properties. TNTs act as excellent photoactive supporting material providing a high surface area, unique directionality for charge separation, and highly effective charge collection.

The presentation will introduce and describe the synthesis of the 2D Mo dichalcogenides, the corresponding physical and electrochemical characterization and encouraging results obtained in HER [4,5], photocatalysis [4-6] and Li-ion batteries [7].

[1] R. Zazpe et al, FlatChem (2020) 21 100166

[2] J. Charvot et al, Chempluschem (2020) 85 576

[3] J. Charvot et al, RSC Adv. (2021) 11 22140

[4] R. Zazpe et al, ACS Appl. Nano Mater. (2021) 3 12 12034

[5] R. Zazpe et al, Appl. Mater. Today (2021) 23 101017

[6] M. Motola et al, Nanoscale (2019) 11 23126

[7] H. Sopha et al FlatChem (2019) 17 100130

11:45am **NS-WeM2-5 Plasma-enhanced Atomic Layer Deposition of Crystalline MoS_2 Thin Films Using a Novel Precursor**, *Jeong-Hun Choi, M. Ha, D. Kim, J. Ahn,* Hanyang University, Korea (Republic of)

Layered two-dimensional molybdenum sulfide (MoS_2) has attracted great interest for a promising candidate material for opto-electronics and photo sensors applications due to its unique characteristics such as tunable bandgap, high electron mobility and high current on/off ratio. In order to apply MoS_2 to the industrial field, significant efforts have been placed in obtaining a wafer-scale uniform MoS_2. Plasma-enhanced atomic layer

deposition (PEALD) is a promising approach for depositing a 2D MoS_2 because of its excellent thickness control. However, the low growth temperature of PEALD makes it difficult to guarantee the quality of the MoS_2 thin films.

In the present study, to overcome this limitation, Cp based molybdenum precursor was used for the PEALD of MoS_2 thin films. This novel precursor with high thermal stability resulted in MoS_2 films with high crystallinity without post thermal treatment.The composition and crystallinity of MoS_2 thin films depends on the PEALD process conditions were investigated by X-ray photoelectron spectroscopy and transmission electron microscopy. Furthermore, through fabricating the field-effect transistors, the potential of MoS_2 for electric device component was investigated.

Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS-WeA2

2D Materials II

Moderators: Suzanne Mohney, Penn State University, Riikka Puurunen, Aalto University, Finland

4:00pm NS-WeA2-11 Controlled Encapsulation of Monolayer MoS$_2$ with Ultrathin Aluminum Oxide for Low Resistance Tunnel Contact Formation, *Alex Henning, S. Levashov, J. Primbs, M. Bissolo, T. Grünleitner, C. Qian, J. Finley, I. Sharp,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany

Seamless integration of two-dimensional (2D) semiconductors with bulk materials is essential for preserving and exploiting their outstanding optoelectronic properties within functional devices. In this respect, ALD has proven to be a critical tool for the dielectric integration of 2D materials by tailoring substrates and interfaces.[1] A major challenge that prevents harnessing the full potential of 2D materials is to contact mono- and few-layer systems with metals without introducing defects or otherwise impeding interfacial charge transport. Here, we demonstrate the encapsulation and doping of monolayer MoS$_2$ with van der Waals (vdW) bonded aluminum oxide (AlO$_x$) and aluminum oxynitride (AlO$_x$N$_y$) by ALD. This is accomplished at low substrate temperature (40 °C) *via* sequential exposure to TMA and ozone or TMA and N$_2$ plasma, respectively. Unique to the field of 2D materials, we utilize *in situ* spectroscopic ellipsometry to assess the effects of adsorbed reactants and film formation on the dielectric function and excitonic properties of a vdW material during ALD, thus allowing optimization of film growth *and* adlayer modulation doping in real-time.

Current-voltage measurements of monolayer MoS$_2$ field-effect transistors (FETs) reveal that the nanometer-thin AlO$_x$ coating increases the carrier concentration (from 1×10^{12} cm^{-2} to 2×10^{13} cm^{-2}), while it also protects MoS$_2$ from defect creation during metallization and processing. Complementary Raman spectroscopy and atomic force microscopy characterization reveal the reversibility of modulation doping induced by the AlO$_x$ adlayer. Encapsulated monolayer MoS$_2$ FETs exhibit a lower contact resistance and an order of magnitude larger maximum drive current, I$_{ON}$. By alleviating the effects from the contact interfaces, we were able to reliably determine a field-effect room-temperature mobility of ~10 cm^2/Vs for the applied monolayer MoS$_2$, synthesized by chemical vapor deposition on a large scale (6Carbon Techn.).

Overall, this work demonstrates the scalable and damage-free encapsulation and doping of 2D materials with weakly bonded and ultrathin AlO$_x$ and AlO$_x$N$_y$ by ALD near room temperature, as well as the fabrication of tunnel contacts, readily compatible with polymer and lift-off processing. Beyond the demonstrated application as a contact interfacial layer, the nanometer-thin conformal coatings are potentially relevant for surface functionalization in chemical sensors and modulation doping of 2D and organic materials implemented in optoelectronic devices.

[1] Grünleitner, T.; Henning*, A.; Bissolo, M.; Kleibert, A.; Vaz, C.A.F.; Stier, A.; Finley, J.J..; Sharp*, I.D.: *Adv. Funct. Mater.* 2022, 2111341.

4:15pm NS-WeA2-12 Synthesis of Crystalline Tungsten Disulfide Using Atomic Layer Deposition and Post-Deposition Sulfur Annealing, *Kamesh Mullapudi, R. Addou,* Oregon State University; *C. Dezelah, D. Moser, J. Woodruff, R. Kanjolia,* EMD Performance Materials; *J. Conley Jr.,* Oregon State University

2D transition metal dichalcogenides have attracted interest in recent years for their unique optical and electrical properties. Tungsten disulfide (WS$_2$)in particular, has gained attention for its applications as channel material for next generation FETs[1] and catalysis.[2] Popular methods such as mechanical exfoliation and chemical vapor deposition have been demonstrated to synthesize crystalline films with grain sizes of up to a few microns and show good electrical properties, but lack scalability and precise layer thickness control, respectively.[3] Atomic layer deposition (ALD) is an ideal technique for achieving highly conformal and uniform films with the layer by layer thickness control needed for these applications, but faces challenges in achieving high crystallinity. Recent work on ALD WS$_2$ has achieved films with superior electrical properties by improving film crystallinity, either by inducing substrate inhibited growth[4]or by post-deposition annealing.[5] However, growing crystallites of the order of a few microns remains a challenge and new processes are needed.

In this work, we report ALD of WS$_2$ using bis(t-butylimido)bis(trimethylsilylmethyl)tungsten (WSN-4) and H$_2$S. 200 cycles of a 1/5/10/0.1/5/10 s WSN-4/soak/N$_2$/H$_2$S/soak/N$_{-2}$ pulse sequence shows film growth at temperatures above 290 °C. Grazing incidence x-ray diffractograms of as-deposited films show a strong peak at 13.9° near the dominant 14.32° (002) peak of 2H polytype of WS$_2$. While no characteristic Raman signal is seen for as-deposited films, x-ray photoelectron spectroscopy reveals the presence of sulfur-deficient WS$_2$ at 290 °C with improved film quality at a deposition temperature of 350 °C. Post-deposition elevated temperature anneals in elemental sulfur produce a significant improvement in crystallinity at temperatures as low as 600 ºC, with SEM images revealing multi-layered WS$_2$ pyramids with sizes of up to ~ 1 µm. The presence of WS$_2$ in sulfur-annealed films is further confirmed by the signature Raman 2LA(M), E-^{1}$_{2g}$ and A-$_{1g}$ peaks.

Further details on the ALD process, sulfur annealing, and electrical properties will be presented at the meeting.

1. D. Lin *et al.,* in *2020 IEEE International Electron Devices Meeting (IEDM)* (2020), p. 3.6.1
2. D. Voiry, *et al.,* Nat Mater **12**, 850 (2013).
3. M. Mattinen *et al.,* Adv. Mater. Interfaces **8**, 2001677 (2021).
4. B. Groven, *et al.,* Chem. Mater. **30**, 7648 (2018).
5. H. Yang *et al.,* Research **2021**, (2021).

4:30pm NS-WeA2-13 In-Situ-Prepared Protective Seed Layer by Plasma ALD on Graphene, *S. Riazimehr,* Oxford Instruments Plasma Technology, Germany; *A. Esteki,* RWTH Aachen University, Germany; *M. Powell,* Oxford Instruments Plasma Technology, UK; *M. Otto, G. Rinke, Z. Wang,* AMO GmbH, Germany; *A. Omahony,* Oxford Instruments Plasma Technology, UK; *M. Lemme,* RWTH Aachen University, Germany and AMO GmbH, Germany; *R. Sundaram,* Oxford Instruments Plasma Technology, UK; *Harm Knoops,* Oxford Instruments Plasma Technology, Netherlands

In this work, we describe a novel method to deposit high-κ dielectrics on graphene through an in-situ-prepared protective aluminum nitride (AlN) seed-layer. The process is performed in an Oxford Instruments Atomfab™ plasma ALD system.[1] Short and low power remote plasma conditions were used to directly grow a thin layer of AlN on graphene, followed by deposition of high-quality aluminum oxide (Al$_2$O$_3$) by remote plasma ALD.

For the development of graphene-based devices, such as transistors, photodetectors, or optical modulators, a deposition of a high-quality dielectric film on graphene is required. However, this deposition is challenging because nucleation on pristine graphene is difficult. While defect-induced nucleation, for example through plasma exposure, improves nucleation, it also decreases the quality of the graphene layer. Recently we reported dielectric deposition using remote plasma ALD, without observable damage, by protecting the graphene by hexagonal boron nitride (hBN).[2] However, using hBN involves additional transfer processes, which may complicate the fabrication and introduce contamination, defects, and wrinkles.

Inspired by this process, we developed a new process using an in-situ deposited AlN seed-layer to protect the graphene effectively, which enables plasma-assisted deposition of Al$_2$O$_3$ without damaging the graphene. Raman measurements demonstrate that the wafer encapsulated by PEALD without AlN shows damage to the graphene, while the wafer protected by the AlN seed layer shows negligible damage. This result confirms that a thin layer of AlN provides sufficient protection for the graphene against the O$_2$ plasma in the subsequent Al$_2$O$_3$ deposition step. The N$_2$ based plasma conditions for the AlN layer were such to allow AlN growth but not lead to observable damage to the graphene. In this contribution, we will furthermore discuss electrical and device properties for this scalable wafer-level production method.

References:

1. Knoops et al., JVST A 39 (6), 2021
2. Canto et al., Adv. Mater. Technol. 6 (11), 2021

4:45pm NS-WeA2-14 Polycrystalline MoS$_2$ Thin Films at 100 °C by Plasma-Enhanced Atomic Layer Deposition, *Miika Mattinen*, M. Verheijen, Eindhoven University of Technology, The Netherlands; F. Gity, E. Coleman, R. Duffy, Tyndall National Institute, University College Cork, Ireland; E. Kessels, Eindhoven University of Technology, The Netherlands; A. Bol, University of Michigan, Ann Arbor and Eindhoven University of Technology

Transition metal dichalcogenides (TMDCs), such as MoS$_2$, are 2-dimensional materials that exhibit vast potential in a variety of applications due to their unique and favorable electronic, optical, and mechanical properties. However, synthesis of uniform, high-quality TMDC films under application-relevant conditions remains a challenge. The most commonly used CVD processes operate at high temperatures that are incompatible with many substrates and applications. For example, typical plastic substrates used for flexible electronics can only withstand temperatures up to about 150 °C.[1] As a result, using ALD to prepare TMDC films is being pursued actively.[2,3] In this contribution, we show deposition of polycrystalline MoS$_2$ (c-MoS$_2$) thin films at temperatures down to 100 °C using plasma-enhanced ALD (PEALD). To date, this is the lowest temperature process reported for c-MoS$_2$ films using any chemical gas-phase method. Building on an existing PEALD process using Mo(N^{t}Bu)$_2$(NMe$_2$)$_2$ and mixed H$_2$S/H$_2$/Ar plasma as precursors,[4] we have identified H$_2$ content in the plasma feed gas as a crucial parameter in controlling the composition and properties of MoS$_x$ films. Based on thorough film characterization, we find that adding H$_2$ in the plasma helps avoid excess S incorporation at low temperatures. The correct stoichiometry, in turn, enables crystallization of MoS$_2$. By increasing the plasma feed gas H$_2$ content to 80%, we are able to deposit polycrystalline MoS$_2$ films at temperatures as low as 100 °C, compared to a minimum temperature of 300 °C without any H$_2$. We have further demonstrated the generality of the approach by depositing TiS$_2$ and WS$_2$ films at lower temperatures than those achieved previously without added H$_2$. Besides crystallinity, the feed gas H$_2$ content is found to control growth rate, film morphology, and electrical properties. For example, electrical conductivity can be varied by at least four orders of magnitude. Thus, the PEALD process enables tailoring MoS$_x$ films to meet the requirements of different applications, such as flexible electronics (low-temperature c-MoS$_2$) and electrocatalysis (a-MoS$_x$).

1 Yao and Gang, *J. Appl. Phys.* **2020**, 127, 030902
2 Mattinen et al., *Adv. Mater. Interfaces* **2021**, 8, 2001677
3 Kim et al., *Adv. Mater.*, **2021**, 20059074 Sharma et al., *Nanoscale*, **2018**, 10, 8615

5:00pm NS-WeA2-15 Selectively Decorated Pt Nanoparticle on WS$_2$ by Atomic Layer Deposition for High-Performance Gas Sensor, *Dain Shin*, School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of); T. Nakazawa, TANAKA Kikinzoku Kogyo K.K., Isehara Technical Center, Japan; I. Sohn, S. Chung, H. Kim, School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of)

Two-dimensional transition metal dichalcogenides (2D TMDCs) have attracted much attention in many research fields owing to their remarkable electrical, chemical, and optical properties. In addition, 2D TMDC-based gas sensor indicates significant gas detection characteristics at room temperature, opposed to the oxide-based sensor which requires external heating for gas detection.[1] Therefore, various 2D TMDC gas sensor studies have been conducted, and as the use of gas sensor expands, performance improvement becomes the challenge of TMDC gas sensors.

Sensing characteristics of 2D TMDC can be enhanced via functionalizing with a noble metal such as Pt, Au, Pd. Among them, Pt is known as a highly effective oxidation catalyst, and Pt nanoparticles (Pt NPs) can make sensing surface more sensitive to gas molecules owing to electronic sensitization and spillover effects.[2] In contrast, as the Pt NPs are difficult to form, atomic layer deposition (ALD) is used to precisely control atomic-scale deposits.

In this study, ALD Pt decorated tungsten disulfide (WS$_2$) was used as a sensing channel to maximize the response of the gas sensor. Pt NPs preferentially grew at higher surface energy point such as dangling bonds and grain boundaries of WS$_2$. Then, sensing characteristics of selectively decorated on WS$_2$ gas sensor was evaluated by various gases. It showed that the NO$_2$ response extremely increased with the number of ALD cycles. However, when the Pt film was formed at the increased number of cycles, the response decreased due to the loss of the semiconducting property of WS$_2$. Thus, we could investigate the proper number of cycles for maximizing the sensing response. In addition, it showed that the selectivity of the gas sensor could also be improved by the ALD Pt process.

References

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