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 ($(CH_3)_2Al(OC_3H_7)$)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 CO_2 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 $i\text{BuPH}_2$ 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,*

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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.

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HM+EM+NS-MoP-8 Flexible and Conductive Zinc oxide – Zincone Nanolaminate Thin Films Deposited using Atomic and Molecular Layer Depositions, *Seung Hak Song,*

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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 Al_2O_3 in Polybutylene Succinate Films

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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_3distribution 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

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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

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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

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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_6H_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 Molecuar 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).

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