

Thin Film

Room: 307 - Session TF-ThA

Thin Film for Permeation Barriers and Membranes

Moderator: Adriana Creatore, Eindhoven University of Technology

2:20pm **TF-ThA1 Enhancing Water Desalination Membranes by Initiated Chemical Vapor Deposition (iCVD), Karen Gleason,** Massachusetts Institute of Technology **INVITED**

The process of iCVD (initiated Chemical Vapor Deposition) is compatible with the fragile polymeric membranes utilized in seawater desalination, since no solvents or high surface temperatures are employed. The iCVD method is scalable over large areas (commercial reactors >1 m across) and to roll-to-roll processing. Over 70 different monomers have been successfully surface polymerized with iCVD.

Two applications of iCVD to water desalination membranes will be discussed. First, iCVD layers have been directly applied to reverse osmosis (RO) membranes for prevention of fouling by molecules and microbes. Second, iCVD enables the deposition of conformal hydrophobic fluoropolymers which are desired for fabricating high performance membranes for desalination by membrane distillation (MD).

The motivation for the antifouling layers is that with the build-up of scale and/or biofilms, system performance declines, resulting in increased operating costs. Fouling also necessitates periodic shutdown for cleaning and replacement of system components and expensive membranes, resulting in higher maintenance costs. Antifouling surface chemistries synthesized by iCVD include amphiphilic and zwitterionic copolymers. Ultrathin (~20 nm) iCVD coatings have been proved to significantly reduce fouling on commercial reverse osmosis (RO) membranes retaining their water permeation and salt rejection performance. The synthesis of iCVD polymer films starts from the membrane surface allowing chemical design strategies for forming grafted interfaces. These grafted interfaces greatly enhance the durability of iCVD surface modification layer which is essential for real-world implementation that would help ensure reliable and economical clean water production.

3:00pm **TF-ThA3 Pulsed Plasma Enhanced Chemical Vapor Deposition for Nanoscale Control of the Size, Shape and Surface Properties of Asymmetric Membranes, Sanket Kelkar, D. Chiavetta, C.A. Wolden,** Colorado School of Mines

The objective of our research is to develop a simple and scalable approach for modification of size and geometry of model membrane supports to fabricate nanopores. In this work, we first employ relatively large template structures (~100 nm) produced by track-etching or e-beam lithography. The pore size is then reduced to the desired level by deposition of material using pulsed plasma enhanced chemical vapor deposition (PECVD). Pulsed PECVD has been developed as a high throughput alternative to atomic layer deposition (ALD) to deliver self-limiting growth of thin films. Pulsed PECVD has two growth components that act sequentially: ALD-like component during the plasma off step ($\gamma \sim 0$); and PVD-like growth component during the plasma on step ($\gamma \sim 1$), where γ is the reactive sticking coefficient. The ALD contribution is constant at ~ 1 Å/pulse whereas the PVD contribution can be typically varied from 0.5 - 10 Å/pulse by appropriate control of operating conditions. The degree of conformality in pulsed PECVD can thus be engineered by controlling the relative contribution of these 2 growth components. Like ALD, pulsed PECVD provides sub-nm resolution over the pore size. However, pulsed PECVD does not result in perfectly conformal deposition profiles, and as such control of the final nanostructure is more complicated. In this work we develop feature scale modeling tools to predict and design the fabrication of nanostructures, such as asymmetric nanopores, using pulsed PECVD. The model is verified by systematic investigation of deposition profiles on patterned cylinders and trenches through cross-section electron microscopy. Polymeric track etched membrane supports (TEMS) are employed as model template structures to demonstrate the capability of pulsed PECVD for precise pore size reduction. Permeance and solute rejection measurements demonstrate that the pulsed PECVD coated TEMS exhibit higher selectivity without compromising on the flux due to their asymmetric structure. These nanoporous membranes will be utilized to study the effect of pore size and geometry on hindered transport of ions and macromolecules at the nanoscale. Furthermore, the hydrophobicity of polymeric supports will be mitigated by deposition of suitable oxide material.

3:20pm **TF-ThA4 A Combined Microstructure Characterization of Moisture Permeation Barrier Layers by Means of Electrochemical Impedance Spectroscopy and Ellipsometric Porosimetry, Alberto Perrotta,** Eindhoven University of Technology; Dutch Polymer Institute (DPI), Netherlands, *S.J. García,* Delft University of Technology, Netherlands, *J.J. Michels,* Holst Centre / TNO, Netherlands, *W.M.M. Kessels, M. Creatore,* Eindhoven University of Technology, Netherlands

In engineering organic electronic devices, encapsulation layers are mandatory due to the sensitivity of active layers and low work function cathodes to moisture. The quality of the moisture permeation barriers is generally validated by means of water vapor transmission rate (WVTR, $\text{gm}^{-2}\text{day}^{-1}$) measurements as well as visual inspection/identification of the local defects (e.g. pinholes) acting as unhindered pathways for water molecules. Furthermore, it has been demonstrated that the water permeation through the nanoporosity - or free volume - of the bulk of the barrier layer can be 15-20 times higher than the one through local defects [1]. While several methods allow the identification of pinholes/defects, novel techniques able to characterize the barrier microstructure in the broad range of nano- and meso-porosity are sought. In a recent work [2], ellipsometric porosimetry has been demonstrated to be a valuable technique for nanopore characterization. Adopting different probing molecules (*i.e.* trivinyltrimethyl cyclotrisiloxane, $d_{\text{V3D3}} = 1$ nm, and water, $d_{\text{H2O}} = 0.3$ nm), a correlation has been found between the (residual) nanoporosity in PE-CVD and (PE-)ALD barriers and their *intrinsic* barrier properties. The pore size range of 0.3–1 nm and its relative content have been found to control the transition in WVTR in the regime of 10^{-4} - 10^{-6} $\text{gm}^{-2}\text{day}^{-1}$. In order to further investigate this range, electrochemical impedance spectroscopy (EIS) has been adopted for the first time in the study of moisture permeation barriers. EIS allows to follow the diffusion of electrolytes through the barrier and cations having different hydrated shell sizes in the range 0.5-0.7 nm, *i.e.* Na^+ , Li^+ , K^+ and Cs^+ , have been selected. Changes in the barrier layer resistance have been attributed to the formation of conductive pathways due to the ion diffusion and allow to study differences in layer porosity in the above-mentioned pore diameter/cation size range. Moreover, it is possible to investigate the water permeation as a function of the variation of the barrier capacitance value upon immersion in the electrolyte solution. In this way, the water uptake (ϕ , the volume fraction of water in a coating) and diffusivity coefficient (D) of different moisture barriers are determined. ϕ and D values in the range of 0.8-4% and 10^{-13} - 10^{-15} cm^2s^{-1} have been found, respectively. This demonstrates that EIS is a versatile tool for the characterization of moisture permeation barriers.

[1] J. Affinito *et al.* 47th Annual Technical Conference Proceedings (2004) 563

[2] A. Perrotta *et al.*, *Microporous and Mesoporous Materials* (2014) 163

4:00pm **TF-ThA6 Influence of Surface Topography and Defects on the Performance of Nanoscale Thin Film Moisture Permeation Barriers, Sean King, D. Jacob, B. Colvin, D. Vanleuven, J. Kelly,** Intel Corporation

Nanoscale moisture permeation barriers are needed for a wide range of applications including encapsulation of organic light emitting diodes, passivation of thin film photovoltaic devices, low dielectric constant Cu interconnect capping layers, hermetic food packaging, and protective coatings for biomedical devices. A variety of materials deposited by various methods have been proposed and successfully demonstrated for these diverse applications. However, it is well known (although not rigorously characterized) that surface roughness and surface particulates/defects can dramatically reduce the permeation barrier performance of all coating materials. In this presentation, we specifically investigate the impact that surface topography and defects can have on the moisture permeation barrier performance of various materials deposited by common methods such as atomic layer deposition (ALD), plasma-enhanced ALD (PEALD), and plasma-enhanced chemical vapor deposition (PECVD). We show that in the absence of significant surface topography a variety of different PECVD, PEALD, and ALD materials can serve as excellent moisture permeation barriers at thicknesses < 10 nm, but the controlled introduction of surface topography dramatically reduces the barrier performance in all cases. To simulate the presence of surface particulates and defects in a controlled manner, various barrier materials of interest were deposited on hanging trenches etched into nano-porous inorganic silicates deposited on a thick moisture absorbing SiO_2 film used for moisture permeation detection. The aspect ratios and dimensions were varied to probe the impact of surface particulates of different size and geometry. It will be shown that increasing surface topography generally increases the minimum thickness for a given material and deposition method to serve as a robust moisture permeation barrier. Over all, the surface topography barrier performance is found to

strongly correlate with the step coverage and conformality of the deposition process with ALD and PEALD films out performing PECVD films.

4:20pm **TF-ThA7 Atomic Layer Deposition for Encapsulation and Barriers**, *F. van den Bruele, F. Grob, Paul Poodt*, Holst Centre / TNO, Netherlands

Developments in the field of flexible electronics, such as organic light emitting diodes (OLEDs), organic photovoltaics (OPV) and other thin-film solar cells, are slowly but surely evolving from lab-scale to industrial production. Proper encapsulation of these moisture sensitive devices is critical, as exposure to moisture from the ambient will degrade these devices, reducing their efficiency, lifetime, or even lead to failure altogether. Especially for OLEDs, the barrier requirements are very challenging, with a Water Vapor Transmission Rate $< 10^{-6}$ g/m²/day. Encapsulation of flexible devices is even more challenging as the encapsulation should not affect the device flexibility too much. Various flexible thin film encapsulation techniques have been recently developed, often combining one or more thin inorganic diffusion barrier layers (e.g. SiN_x, Al₂O₃) with an organic layer. To achieve these very low WVTRs, very high quality barrier layers are required, being pinhole free over the entire device area.

One approach to make high quality inorganic barrier films is Atomic Layer Deposition (ALD). ALD is a deposition technique capable of producing ultrathin conformal films with control of the thickness and composition of the films at the atomic level. With thin (5-100 nm) Al₂O₃ films deposited by ALD, excellent barrier films (WVTR $\sim 10^{-6}$ g/m²/day) can readily be obtained on lab-scale. The major drawback of ALD, however, is its low deposition rate making compatibility with industrial scale processing of devices challenging. The recent development of roll-to-roll and large-area Spatial ALD technology has however spurred the interest in ALD for encapsulation and barriers and the first commercially available electronic devices with ALD encapsulation are probably not far away.

The recent developments of ALD for thin-film encapsulation will be reviewed from a point of view of material- and process development, as well as ALD equipment, with a strong focus on spatial ALD. However, producing barriers with ALD is more complex than only the deposition step itself. For this reason, special attention will be given to aspects such as up-scaling, substrate handling and planarization, managing the effects of particles, characterization and costs of the process.

4:40pm **TF-ThA8 Lifetime of Atomic Layer Deposited Al₂O₃ and Parylene Bilayer Encapsulation for Passive and Active Neural Interfaces**, *Loren Rieth, R. Caldwell, X. Xie, F. Solzbacher*, University of Utah

Encapsulation of penetrating neural interfaces with complex geometries is one of the greatest challenges to achieve long-term functionality and stability need for therapeutic systems. We present results from testing a novel encapsulation scheme that combines atomic layer deposited (ALD) Al₂O₃ and Parylene-C for biomedical implants with integrated electronics. The ALD alumina is utilized for its very low water vapor permeation rate, and the Parylene acts as a kinetic barrier to prevent dissolution of the alumina and as a well-regarded biocompatible coating.

Our devices were first coated with a combination of 52 nm of Al₂O₃ deposited by PA-ALD at 120 °C. The organo-silane adhesion promoter A-174 was applied, followed by a 6-μm film of Parylene-C deposited using a CVD process. Acceleration conditions included temperature and/or voltage bias with interdigitated electrodes (IDEs) and Utah Arrays. IDE testing focused on the effects of additional topography on the encapsulation lifetime at acceleration temperatures up to 80 °C. Topography was added by attachment of 0402 surface mount capacitors and custom 5.5 mm wire-wound Au coils, both used in our fully wireless neural interfaces. A >50% decrease in lifetime from > 280 days to 140 days was measured with the addition topography. We are investigating the mechanism for the decreased lifetime to determine if it is associated with chemical degradation, contamination, or mechanical forces through a comparison with thermal cycling measurements.

In-vitro measurements of the impedance stability for passive UEAs have been used to test the encapsulation performance of these devices while soaking in phosphate buffered saline (PBS). The impedances of these arrays are widely reported to decrease during soak testing due to water ingress. Contrary to this trend, we saw an increase in the impedance of arrays from median impedances of 60 kΩ to 160 kΩ during soaking for 960 days of equivalent time at 37°C. The mechanism for the increase impedance is likely the loss of tip metal.

The impact of voltage bias was also investigated using IDEs and fully-integrated wireless neural interface systems. These devices were maintained 37 °C or higher temperatures for acceleration, and a continuous 5 V bias. For the fully integrated wireless devices, the bilayer encapsulated devices continued to function for 140 days (37 °C equivalent) compared to > 1860

days of equivalent soaking for unpowered devices, indicating ~ 10 times shorter lifetimes. The lifetime is also more than 10x longer than devices only encapsulated with Parylene-C, indicating the bilayer encapsulation is a significant improvement for these very challenging conditions.

5:00pm **TF-ThA9 Influence of Polymer Microstructure and Process Temperature on the Formation of Tailored ALD Coatings on Polymers**, *R.P. Padbury, Jesse Jur*, North Carolina State University

Atomic layer deposition is a technique that is able to integrate nanoscale inorganic coatings to organic polymers. Through this process a number of different inorganic coating morphologies are able to form during ALD nucleation on a wide variety of polymers. In this work, we provide a systematic analysis of the ALD nucleation characteristics on polymers by investigating the influence of polymer microstructure and ALD process temperature. Specifically, in-situ quartz crystal microgravimetry is employed to understand the nucleation behavior of trimethyl aluminum (TMA) in a series of polyesters and poly-n-methacrylates. The data indicates that the glass transition temperature of the polymer, as influenced by variations in microstructure and process temperatures, has a significant impact on the absorption/desorption characteristics during TMA/water exposures. Finally, we propose potential growth mechanisms and demonstrate adjustments to the ALD process parameters that enable the ability to produce a customized interface for ALD materials growth on polymer substrates.

5:20pm **TF-ThA10 Mechanisms of Moisture and Oxygen Transport through Thin Silica-like Barrier Films Deposited in Atmospheric Pressure Dielectric Barrier Discharge**, *Sergey Starostin*, FOM Institute DIFFER, Netherlands, *B.C.A.M. van der Velden-Schuermans, S. Quan*, FUJIFILM Manufacturing Europe b.v., Netherlands, *A. Meshkova, M.C.M. van de Sanden, H.W. de Vries*, FOM Institute DIFFER, Netherlands

Atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) is attracting steadily growing research interest by having clear benefits in terms of equipment costs, footprint size and possibilities for high throughput in-line processing. However the details of the deposition process and the properties of the synthesized coatings were not studied yet as well as for traditional low pressure PECVD. Recently we have reported that good performing moisture and oxygen silica-like barrier films can be fabricated in atmospheric pressure high current diffuse dielectric barrier discharge [1]. However little is known yet about the dominant gas permeation mechanisms through atmospheric pressure plasma deposited barrier films.

In the present contribution the rates of oxygen and moisture vapor permeation were studied as a function of temperature, film thickness and deposition rate. Activated rate theory was applied to analyze the mechanisms of oxygen and moisture transport through the bilayer system of silica-like film and polymer foil. The experimental value of the apparent activation energy E_a determines the degree of interaction between permeating gas and the barrier film. If the E_a values of the bilayer are close to the activation energy of the polymer (47 kJ/mol for moisture), this indicates that the gas transport is controlled by large pinholes with limited or no interaction with the silica film. A transition from polymer controlled moisture permeation to a transport through the silica-like film was observed by tracing an increase in the apparent activation energy from 47 kJ/mol to 80 kJ/mol with film thickness from 2 nm to 100 nm. The gas permeation measurements for the films with different thicknesses were complemented by a detailed morphological study carried out with atomic force microscopy (AFM). The evolution from a non-self-affine morphology of the polymeric substrate to a characteristic smooth surface of the deposited silica-like layer was observed as the film thickness increased from 2 nm to 20 nm. In addition film composition was analyzed by XPS and ATR-FTIR, showing inorganic silica-like character of the deposited layers.

[1] P. Antony Premkumar, S.A. Starostin, M. Creatore, H.W. de Vries, R.M.J. Paffen, P.M. Koenraad, M.C.M. van de Sanden Plasma Process. Polym., 7, 635-639 (2010)

5:40pm **TF-ThA11 Scale Dependent Surface Energies Influence Wetting Behaviour on Ultimately Small Topographies**, *Jan Knauf*, Advanced Molecular Films GmbH and RWTH Aachen University, Germany, *L. Reddemann*, Advanced Molecular Films GmbH and Universität zu Köln, Germany, *K. Cheng*, AMF GmbH, Germany, *A. Böker*, DWI-Leibniz-Institute for Interactive Materials, RWTH Aachen University; Lehrstuhl für Makromolekulare Materialien und Oberflächen, RWTH Aachen University, Germany, *K. Reihls*, Advanced Molecular Films GmbH, Germany

For the first time we observe the effect of scale dependent surface energies on a macroscopic wetting phenomenon. We have been able to produce surfaces structured with sub-nm topographies which exhibit liquid wetting

deviating considerably from the behaviour expected from thermodynamic models.

It is known from grazing-incidence X-ray scattering experiments on planar liquid surfaces that surface energy is reduced at very small length scales [1,2]. By deliberately transferring this effect to solid-liquid interfaces it would be possible to create surfaces with distinct wetting characteristics. We have achieved this transfer by preparing defined monolayers of mixed compositions deposited from 1H,1H,2H,2H-perfluoroalkyl thiols of differing chain lengths. As an example, an equimolar binary mixed monolayer from 1H,1H,2H,2H-perfluorodecyl and 1H,1H,2H,2H-perfluorododecyl thiols shows an increase in advancing water contact angle of about 2° compared to the single component monolayers. This increase is considerably less than expected from simple thermodynamic models, as Wenzel's equation of wetting on rough surfaces predicts an advancing angle difference of 7°. We expected that with suitable contacting liquids and tailored topographies the effect of reduced surface energy could be enhanced or even be inverted towards increased surface energies. Thus, it would be possible to manipulate the apparent wetting behaviour of surfaces by creating well-defined ultimately small topographies.

As model system we prepare monolayers from various mixtures of 1H,1H,2H,2H-perfluoroalkyl thiols ($\text{F}_n\text{H}_2\text{SH}$, $n = 6, 8, 10, 12, 14$) of different chain lengths on gold, which have been proven to adsorb randomly on the substrate without forming separated domains. Another crucial feature is the stiff helical conformation that is adopted by fluoroalkyl chains. Thus, sub-nm surface topographies with distinct height differences of 1.2 Å per CF_2 group and chain distances of 5.8 Å are created, which have been characterized in detail by static secondary ion mass spectrometry, dynamic contact angle measurements and ellipsometry. Parameters governing the formation of the final monolayers could be obtained and were shown to vary systematically depending on the thiols employed.

[1] S. Mora *et al.*, Phys. Rev. Lett. **90**, 216101 (2003)

[2] C. Fradin *et al.*, Nature **403**, 871 (2000)

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