Emerging Materials
Room On Demand - Session EM2
Organic-Inorganic Hybrid Materials

EM2-1 Toward Industrially Viable ALD/MLD Nanolaminate Films for Flexible Electronics*, **Jesse Kalliomaki,** T. McKee,* Picosun Oy, Finland

Foldable phones are now a commercially available product, with some manufacturers already several generations into the product cycle. Use of thin film encapsulation solutions (TFEs) in organic electronic manufacturing (OEM) has become more common as they are lighter and enable folding and stretching of a device, unlike conventional encapsulation methods. The commercial demand has created a large driving force to develop the quality, reliability, and process flow integration of TFEs to enable future product iterations. Inorganic films, such as those generally associated with atomic layer deposition (ALD) are vital building blocks for electronic devices due to the variety of properties they offer to a fabrication scheme. One of the main reliability issues TFEs face is that inorganic films are susceptible to crack under mechanical stress, compromising the barrier performance and cutting the lifetime of the device short. [1]

One approach to address this issue is the nanolamination of dense inorganic layers deposited with ALD for enhanced barrier performance, with organic or hybrid molecular layer deposition (MLD) layers to offer enhanced flexibility [2, 3]. To be an industrially viable solution both components of this process need to be scalable to large substrate sizes, have reasonable deposition time and show good stability in ambient conditions. The more studied MLD processes have been shown to be prone to degradation in ambient atmosphere and quickly lose their beneficial properties [4].

We present process development results from a MLD hybrid with several different inorganic linkers deposited in Picosun R-200 advanced ALD reactor on 200 mm Si substrates. The hybrid films analysed with spectroscopic ellipsometer and Drop Shape Analyzer show excellent large area uniformity at OEM friendly temperature of 90 °C. Long term stability was studied with XPS and FTIR in addition to the previously mentioned methods and demonstrates excellent film stability after months of ambient ageing.

Industrially viable MLD processes can be a valuable tool to have in the fields of OEM and flexible electronics. In this work we show that industrial-scale ALD reactors are capable of producing MLD and ALD layers in the same chamber with low thermal budget and that ALD/MLD nanolaminates (Fig 1) can be easily deposited in a single process step on a large-scale substrate, a process that has a potential as a TFE solution.

[1] Steinmann et al. (2018), doi:10.1557/jmr.2018.194

[2] Yoon et al. (2017), doi:10.1021/acsami.6b15404

[3] Jeong et al. (2020), doi:full/10.1080/15980316.2019.1688694

[4] Ruoho et al. (2018), doi:10.1016/j.mtchem.2018.09.004

EM2-2 Antibacterial Alumochitin Thin Films Grown by Molecular Layer Deposition*, **Karina Ashurbekova,** CIC nanoGUNE BRTA , Spain; K. Ashurbekova ,* Dagestan State University, Russian Federation*; A. Muriqi ,* Tyndall National Institute, University College Cork, Ireland*; L. Barandiaran Larrea ,* CIC nanoGUNE BRTA, Spain*; B. Alonso Lerma ,* CIC nanoGUNE BRTA , Spain*; I. Saric,* University of Rijeka , Croatia*; E. Modin,* CIC nanoGUNE BRTA, Spain*; R. Perez-Jimenez ,* CIC nanoGUNE BRTA, IKERBASQUE, Spain*; . Petravic,* University of Rijeka, Croatia*; M. Nolan ,* Tyndall National Institute, University College Cork, Ireland*; M. Knez,* CIC nanoGUNE BRTA, IKERBASQUE, Spain

Natural chitin and chitinoid materials have outstanding physical and biological properties, which inspired us to develop a process for biomimetic chitinoid organic and hybrid organic-inorganic thin film growth by Molecular Layer Deposition (MLD).

Here, we present a new class of organic–inorganic hybrid polymers called "metallosaccharides", based on sugar-type precursors. For a controlled MLD growth, the hexosamine monosaccharide N-Acetyl-D-mannosamine (ManNAc) was coupled with trimethylaluminum (TMA) repetitively in a cyclic manner for the growth of the hybrid organic-inorganic alumochitin thin films.

The self-limiting behavior of the surface reactions and the growth rate were determined by in-situ quartz crystal microbalance (QCM) and X-ray reflectivity (XRR) studies. The QCM measurements revealed a linear mass increase with the number of MLD cycles. The chemical structures of the coatings were studied with ex-situ X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Characterization of the film structure, morphology, and conformality were performed by High-resolution transmission electron microscopy (HR-TEM), showing uniform and conformal alumochitin films wrapping ZrO2 nanoparticles (NPs).

The chemical interaction between ManNAc and TMA, and the possibility of hybrid alumochitin film formation were modeled by density functional theory (DFT). The computed interaction energies between TMA and ManNAc are negative, meaning that there’s a strong interaction between these precursors. Theoretical modeling revealed that the proposed reaction mechanism for the ManNAc/TMA MLD process is energetically favorable.

The evaluation of the antimicrobial activity of the alumochitin thin film against Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli) bacteria was assessed. Bacteria attachment and proliferation on glass substrates, covered with MLD film, were analyzed by confocal microscopy. (Fig. 1S in the ESI) Both types of bacteria grow and proliferate on positive control samples, while neither Staphylococcus aureus nor E. coli bacteria attached to the surface of the alumochitin film. These results show a great antimicrobial activity of alumochitin against gram-positive and gram-negative bacteria, as well as its enormous application potential as bioactive surfaces.

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EM2-3 Mechanics of Flexible ε-Fe_2O_3/Organic Superlattice Thin-Film Magnets*, **Janne-Petteri Niemelä,*** Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; A. Philip, G. Tewari,* Aalto University, Finland*; N. Rohbeck, B. Putz, T. Edwards,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M. Karppinen,* Aalto University, Finland*; J. Michler, I. Utke,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The little-known iron(III)oxide polymorph ε-Fe_2O_3 has risen intrigue for its ferrimagnetic character and high coercive field, that make it an interesting material for magnetic storage applications.[1] To enhance the appeal of ε-Fe_2O_3 thin-film magnets for flexible electronics, tailoring its mechanically rigid character is however desired. Here we demonstrate tailoring of the mechanical properties of ε-Fe_2O_3 thin films through insertion of Fe-terephtalate interlayers by using the combined atomic/molecular layer (ALD/MLD) deposition technique.[2,3]

We deposited ε-Fe_2O_3 oxide films, Fe-terephtalate (Fe-TP) hybrid films and ε-Fe_2O_3/Fe-TP superlattice thin films using $FeCl_3$ as the Fe metal precursor, H_2O as the oxygen source, and terephtalatic acid as the organic precursor.[2,3,4]Nanoindentation experiments indicate that the insertion of the Fe-TP interlayers in the ε-Fe_2O_3 matrix enables a factor-of-two decrease in elastic modulus for the superlattice films down to 70±20 GPa. In-situ tensile fragmentation testing indicates that the crack onset strain and critical bending radius can be tuned by a factor of three.Modeling of the tensile fragmentation patterns through Weibull statistics shows that cohesive and interfacial shear strain, following the trend for crack onset strain, increase with increasing organic content, while gains for the respective strengths are limited by the simultaneous reduction in elastic modulus. Importantly, we demonstrate through magnetization vs. magnetic field (M-H) measurements that the unique magnetic characteristics of ε-Fe_2O_3 are not sacrificed in the superlattices with enhanced mechanical flexibility. Magnetic characterization of strained films indicates absence of catastrophic failure upon fragmentation and modest debonding of the films, while the improved mechanical characteristics for the superlattices translate to improved preservation of the magnetic characteristics.

The present results are interesting for magnetic storage applications in flexible electronics and highlight the potential of the combinatorial ALD/MLD technique for enhancing mechanical properties of—not only inorganic-organic alloys as known from the past[5]—but also of multilayer structures with inorganic layers thick enough to generate usable functionalities.

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EM2-4 Effect of Vapor-Phase Metal Infiltration on Lithography of PMMA Resist for EUV Applications*, **Su Min Hwang**, R. Gummadavelly, D. Le, J. Kim, Y. Jung, J. Veyan,* University of Texas at Dallas, USA*; C. Nam,* Brookhaven National Laboratory*; J. Ahn,* Hanyang University, Korea*; J. Kim,* University of Texas at Dallas, USA

Due to the limitation of resolution with scaling down of feature size, extreme ultraviolet (EUV) was has drawn great attention as the light source for the next-generation lithography process. Unlike the photoresists for UV irradiation, EUV photoresist interacts with secondary electrons. However, the current polymer-based resist has confronted a number of challenges, such as pattern collapsing due to resist thickness, poor EUV adsorption, and etch-selectivity, etc. To circumvent the limitation, research on new materials, particularly metal incorporation with organic resists have been recently reported. With introduction of metal, the hybrid resist can increase the EUV absorption as well as the mechanical stability during the pattern transferring.[2,3] Among the various synthesis of inorganic-organic hybrid EUV resists, vapor-phase infiltration of metal source into existing organic resist using ALD process can be employed. This *ex-situ* process can avoid the complex chemistry and employ the standard fabrication process.

In this work, we have demonstrated the infiltration of Hf into PMMA e-beam resist using ALD process. The PMMA resist is coated on the Si substrate using a spin-coating technique, followed by exposure of TDMA-HF precursor in the ALD chamber at 85 °C. In XPS gas cluster ion beam depth profile, Hf concentration showed 5 to 10 at. % in PMMA film, implying that Hf is distributed in the PMMA resist. Specifically, we investigated the effect of metal-infiltrated resists on electron-induced solubility by understanding the change of chemical bonds using an *in-situ* Fourier transform infrared spectroscopy (FTIR) equipped with electron gun capability. Each sample was exposed with electrons with 100 eV, which was similar energy of incident photons from EUV, and characterized the difference of chemical bonds before and after exposure. Based on these theoretical results, pure PMMA and metal infiltrated PMMA was exposed with a variable dose of electrons, followed the developing test with various solvent to investigate the effect of metal infiltration.

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EM2-5 About the Importance of Purge Time in Molecular Layer Deposition of Alucone Films*, **Hardik Jain**, P. Poodt,* Holst Centre / TNO, Netherlands

The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure. In some cases, however, the purge step is of equal importance, for example in the MLD of alucone films using trimethylaluminum (TMA) and ethylene glycol (EG). These alucone films tend to be porous in nature due to which the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The outgassing of the infiltrated reactant can take relatively very long thereby becoming the deposition rate limiting step. If enough purge time is not provided for the reactant to outgas, it will lead to an undesirable CVD component alongside MLD in the overall growth. We have investigated the MLD of alucone focusing on the effect of purge time of TMA on the growth kinetics. To avoid any negative impact of the CVD component on the deposition rate and the film's properties, we have also developed a kinetic model to correlate parameters like exposure times, partial pressures, purge times and deposition temperature to the CVD component in the growth. With an intention to improve the outgassing efficiency of TMA, the influence of purge gas flow on the CVD growth component has also been briefly investigated. Finally, we show that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration altogether and increase the deposition rate of alucone processes by at least an order of magnitude.

EM2-8 Low Temperature Alumina and Alucone Multistack by Ald for Flexible and Transparent Gas Barrier Layers*, **Shiv Bhudia**, N. Adjeroud, R. Leturq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Gas permeation barriers are widely employed in many technological applications. From medium barrier properties (Oxygen transmission rate, OTR ≈ 1 cc m^{-2} day^{-1} bar^{-1}; Water vapour transmission rate, WVTR ≈ 1 g m^{-2}day^{-1}) as in the food packaging industry. To very high barrier properties (OTR ≈ 10^{-5} cc m^{-2} day^{-1} bar^{-1} ; WVTR ≈ 1 g m^{-2}day^{-1}) such as in flexible organic opto-electronics. Here, it is even more critical to avoid the presence of water and oxygen in the active layer.

Atomic layer deposition (ALD) of amorphous alumina show very promising properties for passivation or encapsulation layer, for gas barrier layers. However, the deposition conditions usually require temperatures above 100 °C or highly oxidative conditions (ozone or oxygen plasma) to obtained reasonable deposition rates and high-density material. And due to its brittle nature, it limits the implementation on rigid or low flexibility substrates. A process for temperature sensitive substrates used in food packaging would be highly welcomed.

In this work, we combined amorphous alumina with alucone, in multi-stack structures on flexible PET substrate for food packaging. The inorganic alumina layer serves as gas barrier layer and the organic alucone layer decouples the adjacent alumina layers, thus avoiding direct passage of the permeant gas through pinholes.

By developing an in-house He permeation tester, we have investigated the physical diffusion of Hellium on these structures; and a method of extracting diffusivity and solubility from different substrate thickness is proposed. To further understand the morphology of these layers, we have simulated those structures using Finite Element Method (FEM).

EM2-11 Transport in Vapor Phase Infiltration Processes: Modeling and Measuring Competition between Reactions and Diffusion*, **Emily McGuinness**, Y. Ren, B. Jean, R. Lively, M. Losego,* Georgia Institute of Technology

Over the past decade, vapor phase infiltration (VPI) has emerged as a technique to create hybrid organic-inorganic materials with a wealth of industrially relevant applications. While the utility of VPI has become clear, the fundamental mechanisms that control the hybrid material structure (and therefore material properties) are complex and not well understood. In this presentation, a reactive-diffusion model is explored that provides insight into how the presence of reactions between polymers and metalorganic precursors modifies the transport behavior of the vapor phase metalorganic molecule through the material. This model is found to not only account for diffusion of the vapor phase metalorganic precursor within the polymer film, but also capture the reaction between the two phases, as well as associated reductions in diffusivity. For example, a hindering factor is established that accounts for the interference of chemically bound precursor with further diffusion of unbound precursor. This parameter captures the orders of magnitude reduction of out-diffusion coefficients as compared to in-diffusion coefficients observed in certain VPI systems. The model is shown to both qualitatively and quantitatively capture and predict VPI behaviors in an experimental case-study of the trimethylaluminum (TMA) / poly(methyl methacrylate) [PMMA] VPI system **(Figure 1)**. Parameters extracted from the model can be used to understand the fundamental thermodynamic and kinetic principles that underly the VPI process. For instance, the Damkohler number (a dimensionless value comparing the rate of diffusion to the rate of reaction in a system) for TMA / PMMA at 130˚C is found to be approximately 0.08. This value indicates that diffusion of TMA occurs faster than reactions between TMA and PMMA under these conditions. As a result of this, the TMA / PMMA system is able to exhibit high mass uptake in early times before hindering of the system sets in from the formation of bound precursor. Overall, this presentation will not only introduce a new model capable of capturing the complexities of VPI, but also provide guidelines and a case-study of its utility in experimental parameterization and prediction.

EM2-14 First Principles Study of Reactions in Hybrid Organic-Inorganic Films: The Impact of the Organic Reactant*, **Arbresha Muriqi**, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

The development of hybrid inorganic-organic films with well-controlled properties is vital for the future of nanotechnology for many applications. Molecular layer deposition (MLD) allows the deposition of hybrid films using sequential, self-limiting reactions, similar to ALD. In this study, we investigate the growth mechanism of different hybrid organic−inorganic thin films by using first principles density functional theory (DFT).

The prototype for MLD hybrid films are composed of thin films of aluminium alkoxides, known as ”alucones”. We investigated the MLD reaction productsbetween the post-TMA Monomethyl-Al_2O_3 ($Al\text{-}CH_3\text{-}Al_2O_3$) and Dimethyl-$Al_2O_3$ ($Al(CH_3)_2\text{-}Al_2O_3$) surface and diol organic precursors, including ethylene glycol (EG) as well as glycerol (GL). The results show that Al–O formation with release of methane is favorable for all diols. Interaction energies show that longer diols will not maintain an upright configuration compared to lying flat and participating in the “double reaction” where the two terminal –OH groups bind to surface TMA. A detailed comparison of ethylene glycol (EG) and glycerol (GL) precursors is presented to assist the interpretation of experimental findings regarding the differences in the hybrid films grown by EG and GL. EG and GL can lie flat and create double reactions through the two terminal hydroxyl groups. This phenomenon removes active hydroxyl sites for EG. For GL the third hydroxyl group is available and growth can proceed. This analysis shows the origin of differences in thickness of alucones found for EG and GL.

We also investigate the growth mechanism of magnesium containing hybrid films known as “magnesicone”from the reaction of EG and GL at MgCp-terminated MgO as a model system. Interaction energies show that while the ligand elimination process is favorable for both precursors, GL species prefers to lie in an upright position and EG prefers to orient in a flat configuration and interacts at the MgO surface, resulting in a thicker GL-based magnesicone compared to the EG-based magnesicone. This is consistent with the experimental findings for magnesicone growth using these precursors.

Finally we study the growth of titanium-containing hybrid organic−inorganic films known as “titanicones”. using titanium tetrachloride ($TiCl_4$) or tetrakisdimethylamido ($Ti(TDMA)_4$) as metal source and ethylene glycol (EG) or glycerol (GL) as organic reactants. This investigation contributes to the understanding of growth process of EG and GL based titanicones at different surfaces and is valuable in supporting experimental data on titanicone film growth.

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