Emerging Materials
Room Grand Ballroom A-C - Session EM1-WeM
Molecular Layer Deposition

Moderators: Stacey F. Bent, Stanford University, Charles L. Dezelah, ASM

8:00am **EM1-WeM-1 Molecular Layer Deposition of Titanicone Films using TiCl and Fumaric or Maleic Acid: Growth Mechanism and Ambient Stability**, ***Yan-Qiang Cao**, A Li,* Nanjing University, China

Atomic layer deposition (ALD) has been widely used for synthesizing a myriad of inorganic materials. With the development of ALD, it was also used to deposit a relatively new class of organic-inorganic hybrid films, called as molecular layer deposition (MLD) due to the molecular nature of the deposition process. Although MLD has prepared some types of organic-inorganic hybrid films, it is still in its infancy now. Compared to inorganic precursors, organic precursors for MLD have much more selections in the functional groups, chain backbone, chain length and molecular structure. Moreover, there are a special group of organic molecules called isomers, which possess the same functional groups and backbones with different structures. To date, the research about organic isomer precursors on MLD growth is rather rare.

Therefore, this work systematically investigated the effect of organic precursors of isomer of fumaric acid (FA) and maleic acid (MA) on MLD growth and stability of inorganic-organic hybrid films of titanicones. Titanicones films were fabricated by MLD using $TiCl_4$ and FA or MA at various growth temperatures. It was found that the *cis-/trans* configurations of organic precursors can influence the MLD growth behavior, the preference for bonding mode and ambient stability of hybrid films. $TiCl_4$-MA and $TiCl_4$-FA MLD processes exhibit quite different growth mechanism. The composition ratio of C : O : Ti of Ti-MA films from X-ray photoelectron spectroscopy (XPS) analyses has little change with deposition temperature, whereas Ti-FA shows the temperature dependent composition. Moreover, both *ex situ* XPS and *in situ* quartz crystal microbalance (QCM) demonstrate that the as-deposited MLD Ti-MA hybrid films are consisted of inorganic Ti-O-Ti units and organic-inorganic Ti-MA units. In addition, density function theory (DFT) calculation was performed to characterize the possible reaction mechanism of $TiCl_4$-MA MLD process. The DFT results are in accordance well with experiment data. Ti-MA and Ti-FA hybrid films show the preference for bidentate and bridging bonding mode, respectively. Furthermore, the inorganic Ti-O-Ti units in hybrid films can improve ambient stability of Ti-MA hybrid films. As a result, Ti-MA hybrid films are much more stable in open air for one year than Ti-FA ones. These results are very important for understanding the MLD process and choosing proper organic precursors.

8:15am **EM1-WeM-2 Temperature Dependent Surface Chemistry in Molecular Layer Deposition of Polyimide on Cu and Si**, ***Chao Zhang**, M Leskelä, M Ritala,* University of Helsinki, Finland

Polyimides (PIs), a class of high-performance polymers widely used in semiconductor industry, exhibit excellent electrical, mechanical and thermal properties[1]. PIs have been originally prepared by solution-cast method. However, solvent-free processes with capability to deposit high-quality PI films with precisely controlled thickness are needed in thin film device fabrication. So, molecular layer deposition (MLD) of PIs as an alternative approach has been getting more attention lately.

In this work, MLD growth of PI was first compared on Cu and Si substrates by using 1,6-hexanediamine (DAH) and pyromellitic dianhydride (PMDA) as precursors at deposition temperatures of 170-220 °C (Fig. 1). At 170-180 °C the PI growth rate on Si is around 5 Å/cycle and close to 4 Å/cycle on Cu. On the other hand, at higher temperatures from 200 to 210 °C much more PI was deposited on Cu with a growth rate of 7-8 Å/cycle whereas only a tiny amount of PI was grown on Si. The significant contrast of the PI growth rate on Cu and Si at 200 °C shows potential for area-selective MLD, which also encourages us to explore further the surface chemistry of PI MLD on Cu and Si. Based on our study with ATR-FTIR, XRD, AFM and XPS a surface reaction mechanism is proposed for the PI growth on Cu and Si at 170 and 200 °C. For the PI MLD on Si (Fig. 2 a), cyclic PI formation can be accomplished via two pathways[2-4]: 1) reversible amidization (step 1) followed by imidization (step 4); 2) the same amidization (step 1) but different imidization with inter-chain polyimide forming as intermediate (step 2, 3). After the rapid amidization there is a competition between the reversed amidization (precursor re-evaporation) and imidization (cyclic PI formation). At 170 °C imidization dominates while at 200 °C reversed amidization dominates resulting in minor PI film growth on Si. On Cu (Fig. 2 b), the resulting films consist of not only cyclic PI but also inter-chain PI since Cu ions can diffuse into the deposited film and further catalyze and/or stabilize the inter-chain polyimide by forming metal-organic complexes with the partially ordered system inside. However, at 170 °C ring-closed imidization seems to dominate, whereas at 200 °C inter-chain PI formation dominates.

References:

[1] G. Maier, Progress in Polymer Science **26,** 3 (2001).

[2] E. Sacher, Journal of Macromolecular Science, Part B **25,** 405 (1986).

[3] J. H. Jou and P. T. J. M. Huang, **24,** 3796 (1991).

[4] E. Spassova, Vacuum **70,** 551 (2003).

8:30am **EM1-WeM-3 Integrated MLD Supercycle for the Direct Deposition of Zeolitic Imidazolate Framework Films**, ***Alexander John Cruz**, I Stassen, R Ameloot,* KU Leuven, Belgium

Intrinsic nanoporosity and synthetic tunability position nanoporous materials, such as metal-organic frameworks (MOFs) at the center-stage of some emerging applications in microelectronics [1]. For example, these materials have shown promising properties for device integration ranging from gas sensing to low-k dielectrics for future logic microprocessors. Essential for capitalizing on the disruptive potential of MOFs on such device-oriented valorization is a solvent-free process for the deposition of ultrathin, defect-free films with unprecedented control over thickness and properties [2]. We herein present an ongoing proof-of-concept study on the direct molecular layer deposition of thermally and chemically stable nanoporous MOF films using a modified commercial ALD/MLD reactor. In our ZIF-8 (zinc-2-methylimidazolate) test case, sequential reactions of diethylzinc, water, and 2-methylimidazole are assembled into a supercycle to yield layer-by-layer deposition of films that are crystalline and nanoporous as-synthesized, in the absence of separate post-deposition treatments. To explore a variety of chemical handles for molecular-level control of the thickness and film characteristics, we introduced modulators such as water, methanol and ethylene glycol during different stages of the supercycle by means of ALD pulses. The present contribution will highlight our most recent works on MLD ZIF-8 and a brief introduction on a catalog of new MOF chemistries *via* integrated ALD-MLD-CVD processes, as well as a demonstration of potential integration routes to applications in microelectronics. Furthermore, we will elaborate the steps on how we took advantage of *in situ* ellipsometry and QCM in combination with complementary *ex situ* techniques for unraveling mechanistic insights into the reaction-crystallization processes. We will clarify and explain optimization guidelines and high-level design rules on how to implement MOF-MLD formulations to other laboratory setups and fabrication facilities.

[1] Stassen, I., Ameloot R., *et al.* An updated roadmap for the integration of metal-organic frameworks with electronic devices and chemical sensors. Chem Soc Rev 46, 3185–3241 (2017).

[2] Stassen, I., Ameloot R., *et al.* Chemical vapor deposition of zeolitic imidazolate framework thin films. Nat. Mater. 15, 304–310 (2016).

8:45am **EM1-WeM-4 Understanding Molecular Layer Deposition Nucleation Mechanisms in Polyurea via Time Domain Thermoreflectance**, ***Rachel Nye**, M Fusco,* North Carolina State University*; E Radue, A Kelliher, P Hopkins,* University of Virginia*; G Parsons,* North Carolina State University

Despite the high utility of molecular layer deposition (MLD) polymer films in applications such as sensors and electronics, the underlying chemistry behind these processes remains unclear. While the effects of active site termination, polymer chain orientation, and monomer absorption are areas of current interest to understanding MLD growth mechanisms, the role of diffusion in polymer films has not yet been considered. This is due to lack of an efficient analytical approach to understanding diffusion mechanisms. To address this issue, we introduce a technique new to the field, time domain thermoreflectance (TDTR), to explore the possibility of monomer diffusion as an alternate growth mechanism to previously reported linear or absorption mechanisms.

Polyurea films are deposited from p-phenylene diisocyanate (PDIC) and ethylenediamine (ED) or hexanediamine (HD) to provide different polymer compositions. Traditional MLD analysis techniques including atomic force microscopy (AFM), spectroscopic ellipsometry, and Fourier Transform infrared spectroscopy (FTIR) are used to characterize surface roughness, growth characteristics, and chemical composition, respectively. AFM results indicate the presence of two different growth regimes based on trends in surface roughness versus cycle number. At small cycle numbers, surface roughness increases with film thickness, indicating nonconformal growth on isolated nucleation “islands”. After approximately 50 cycles (20 nm), surface roughness decreases, indicating conformal film growth due to the convergence of islands. Further investigation into these regimes is performed with picosecond acoustics data from TDTR measurements, which has not previously been available for MLD films. Our results demonstrate that the speed of sound increases with increasing film thickness, hence the film’s density decreases. Both the decrease in density and surface roughness can be explained by monomer diffusion from the surface into the bulk polymer film after the film reaches a certain threshold thickness. These findings provide a basis for understanding and characterizing monomer diffusion in organic/hybrid films, which will ultimately clarify the overall growth mechanisms of MLD processes.

9:00am **EM1-WeM-5 Molecular Layer Deposition of Indicone Thin film using Indium Precursor and Hydroquinone***, **Seung-Hwan Lee**, G Baek, J Lee,* Hanyang University, Republic of Korea*; T Ngoc Van, B Shong,* Hongik University, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Flexible electronics are obtaining attention for potential to be used in various applications because of their light, thin, conformable design advantages.[1] However, most inorganic materials have limitations to be used for flexible devices due to high elastic modulus and weakness on external stress or strain, regardless of their superior electrical properties. On the other hand, organic materials are often elastic so that they are resistant to external stress or strain, but with poor electrical performance. Therefore, hybrid materials combining advantages of organic and inorganic materials are are of much research interest. Molecular layer deposition (MLD) is a promising technology for deposition of organic and organic-inorganic hybrid thin films for conformality and excellent thickness controllability.[2] In this work, indicone thin films containing indium and organic diol linkage are deposited by MLD. [1,1,1-trimethyl-N-(trimethylsilyl)-silanaminato]-indium (InCA-1) and hydroquinone (HQ) are used as the indium and the organic precursor, respectively, at deposition temperature between 100-250℃. The MLD properties are demonstrated from growth behavior; Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) are used to analyze the chemical characteristics in the material. Density functional theory (DFT) calculations are utilized to investigate the chemical mechanism of the deposition reaction. Indium-based hybrid films are grown by supercycles of indium oxide atomic layer deposition (ALD) and indicone MLD. Structural, optical and electrical properties with respect to the super-cycle ratio are investigated. As the fraction of indicone incorporated in the hybrid films increases, crystallinity decreases while electrical resistivity increases. The hybrid film, which has 99:1 indium oxide and indicone ratio, shows slightly increased resistivity, but shows enhanced resistance toward mechanical deformation compared to pure ALD indium oxide thin films. The hybrid film has superior mechanical property for future flexible devices.

[1] Y. Sun, J.A. Rogers, Inorganic semiconductors for flexible electronics, Advanced materials (2007), 19(15), 1897-1916.

[2] Steven M. George et al, Growth and properties of hybrid organic-inorganic metalcone films using molecular layer deposition techniques, Advanced Functional Materials, (2013), 23, 532

9:15am **EM1-WeM-6 Air Stable Alucone Thin Film Deposited by Molecular Layer Deposition using Hetero Bifunctional Organic Reactant***, **GeonHo Baek**, S Lee, J Lee, J Park,* Hanyang University, Republic of Korea

Molecular layer deposition (MLD) is fundamentally a modified Atomic Layer Deposition (ALD) principle, where conformal thin films are fabricated with self-limiting surface reaction chemistry. The ALD/MLD hybrid process makes it possible to deposit thin film by in-situ process only by changing the precursor and to manufacture excellent organic-inorganic hybrid thin films. Many researcher groups reported “metalcone” films using various metal and organic precursors but there are not many studies on hetero bifunctional group organic precursors. [1] Because of its two different functional groups, it has different thin film properties, and this reinforces the moisture-sensitive problems of most MLD films. Therefore, it will be very useful in the application field of the organic thin film.

In this work, we fabricated alucone thin films using Trimethylaluminum (TMA) and 4-mercaptophenol(4MP) by MLD and the properties of the thin films were analyzed as annealing progressed with increasing temperature. In particular, we observed the alucone film characteristics from 4MP with different functional groups of -OH and -SH group. Growth per cycle tends to decrease due to the difference in reactivity between the -OH and the -SH group but it forms a denser thin film due to the bonding angle close to 90° when bonded to the -SH group. XPS analysis confirmed that some elements including S were reduced during the annealing and SE analysis indirectly confirmed that the film was dense by increasing the refractive index. Annealed alucone film was occurred thermal polymerization in the high temperature region and carbon ring structure trans the graphene flake by graphitization. Raman and XPS analysis carried out various characterization related to carbon. At the annealing temperature of 750°C, the resistance can be measured while changing from insulator to conductor. Annealed MLD alucone thin film as a hybrid semiconducting material has various potential applications such as electronic, capacitor or thermoelectric devices.

reference

[1] Steven M. George et al, Growth and properties of hybrid organic-inorganic metalcone films using molecular layer deposition techniques, Advanced Functional Materials, (2013), 23, 532

9:30am **EM1-WeM-7 Molecular Layer Deposition of “Magnesicone”, a Magnesium-based Hybrid Material, as a Matrix Material for Solid Composite Electrolytes***, **Jeroen Kint**, F Mattelaer, M Minjauw,* Ghent University, Belgium*; P Vereecken,* IMEC, Belgium*; J Dendooven, C Detavernier,* Ghent University, Belgium

Porous thin films are a very versatile class of materials for a wide range of applications due to their high (reactive) surface area. Numerous deposition methods are available, yet when conformality on complex 3D structures and sub-nm uniformity and thickness control and are requirements for the envisioned application, these deposition methods often don’t meet these demands. Atomic and molecular layer deposition (ALD/MLD) are generally accepted as the go-to methods when conformality, uniformity and sub-nm thickness control are necessary conditions. When the application requires porous films, organic/inorganic hybrids (metalcones) can be deposited using MLD, and with a post-treatment, they can be made porous. This has already been shown for alucones. A wide variety of these metalcones exist, yet no Mg-based flavours are available. In this work, MLD and a post-deposition anneal were used to obtain porous MgO thin films.

A novel magnesium-based organic-inorganic hybrid process was developed using magnesium bis-(methylcyclopentadienyl) and ethylene glycol or glycerol. The growth characteristics of both processes were characterized using in-situ ellipsometry. For both flavours of the magnesicone, saturated growth could be achieved in a broad temperature window (100-250°C). The hybrid nature of these films was confirmed using FTIR and EDX. Exposure of these “magnesicone” films to ambient atmosphere was investigated using FTIR. Both flavours reacted with ambient air, absorbing water.

As deposited magnesicone films were annealed in oxidizing ambient at different heating/cooling rates, while being monitored using real-time spectroscopic ellipsometry (RTSE). The influence of the heating/cooling rates on pore formation was extracted from the changes in refractive index (linked to the density) and the film thickness. Three regimes could be discerned. Firstly, moderate heating/cooling rates lead to porous films (corresponding to a sudden drop in density and increase in porosity). Secondly, it was observed that pores collapse when a rapid cool-down takes place, as seen from an increase in density and a decrease in thickness. Finally, heating at high ramp rates causes no pore formation. These findings were backed up by subsequent ellipsometric porosimetry measurements. For high ramp rates (≥400°C/h), no pores were formed, whereas at lower ramp rates (≤200°C/h) pore formation was confirmed.

A novel process for the deposition of a magnesium-based hybrid organic-inorganic material, “magnesicone” was developed. It’s response to different annealing conditions was investigated using RTSE and EP. By doing so, porous MgO films with porosities up to 45% could be achieved.

9:45am **EM1-WeM-8 Molecular Layer Deposition of Polyamide Films on Particles Using a Rotating Cylinder Reactor***, **Tyler Myers**, S George,* University of Colorado - Boulder

Molecular layer deposition (MLD) utilizes sequential, self-limiting surfaces reactions to deposit polymeric thin films. Depending on the precursors, the MLD polymeric film can be all-organic or a mixed organic-inorganic hybrid film. In this study, all-organic polyamide MLD films are deposited on particles using adipoyl chloride and ethylene diamine as precursors. This polyamide MLD film is designated as Nylon 6,2. The MLD is performed in a rotating cylinder reactor to agitate the particles. The rotating cylinder reactor is also located inside an isothermal enclosure to eliminate cold spots that cause difficulties when using low vapor pressure precursors.

The polyamide MLD was performed at low temperatures ranging from 37°C to 80°C. These low temperatures allow the polyamide MLD film to be deposited on thermally sensitive organic particles such as pharmaceutical particles. Using witness wafers in the reactor, the sequential adipoyl chloride and ethylene diamine exposures led to a growth rate of 4 Å/cycle at 67 °C for the Nylon 6,2 MLD film as determined by x-ray reflectivity (XRR) measurements. These growth rates were in good agreement with the film thicknesses measured by transmission electron microscopy (TEM) on inorganic particles (ZrO_2 and TiO_2) and organic particles (cellulose and active pharmaceutical ingredients) (See Supplemental Figure 1). The polyamide MLD growth rates were inversely dependent on temperature as observed earlier for previous polyamide MLD and alucone MLD film growth.

The TEM images revealed that the polyamide MLD films were smooth and conformal on the various particle substrates (See Supplemental Figure 1). Fourier Transform Infrared (FTIR) vibrational analysis of the polyamide MLD films revealed the presence of N-H, C-H, C-N, and C=O stretching vibrations and CO-N-H bending modes. X-ray photoelectron spectroscopy (XPS) analysis on witness wafers yielded peaks corresponding to C, N, O, and a small amount of Cl. Energy Dispersive Spectroscopy (EDS) mapping of the polyamide MLD film grown on cellulose particles observed N and Cl in the polyamide coating. The deposition of all-organic polymer MLD films on particles may have many interesting applications because of their high elasticity and chemical stability.

Author Index

Bold page numbers indicate presenter