Emerging Materials

Room Arteveldeforum & Pedro de Gante - Session EM-MoP

Emerging Materials Poster Session

EM-MoP-5 First Principles Modelling of Growth of Hybrid Organic-Inorganic Films*, **Arbresha Muriqi**, M Nolan,* Tyndall National Institute, Ireland

Organic-inorganic hybrid materials are a unique class of materials with unique properties which means they are useful in flexibile devices. Molecular layer deposition (MLD) offers novel pathways for the fabrication of such hybrids by using metallic precursors and a vast range of organic precursors. To investigate and understand the mechanism of growth and stability a combination of theoretical and experimental data is needed.

In this contribution, we present a first principles investigation of the molecular mechanism of the growth of hybrid organic−inorganic thin films of aluminium alkoxides, known as ”alucones” grown by MLD. We focus on the interactions between precursors and this is explored by analyzing the MLD reaction products between 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 the organic precursors ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG) and tetraethylene glycol (FEG). The energetics of the reaction of alumina with ethylene glycol (EG) and glycerol (GL) precursors are also investegated in detail to assist the interpretation of experimental findings regarding the differences in the hybrid films grown by EG and GL. The DFT calculations show that while the organic precursors can bind to the TMA fragements via formation of Al-O bonds and loss of CH_4, it is most favorable for the organic precursors to lie flat and create so-called double reactions through two terminal hydroxyl groups with the surface fragments, where the terminal groups bind to Al. For EG this potentially removes all the active sites and growth will be less favourable. For GL the third hydroxyl group is available and growth can proceed. We also showed that the TMA in the next pulse reacts favourably with this OH from GL. The longer the chain length the harder it is for the organic precursor to stay straight and not create double reactions. This investigation contributes to the understanding of growth process of EG-alucones and GL-alucones at the molecular level and is valuable in supporting experimental data on hybrid film growth.

EM-MoP-7 Thermal Atomic Layer Deposition of Aluminum Nitride using a Liquid Aluminum Dihydride Complex and Ammonia*, J Choi, D Ma, J Kim,* UP Chemical Co., Ltd., Republic of Korea*; T Chowdhury, R Hidayat, H Kim, W Lee,* Sejong University, Republic of Korea*; **Wonyong Koh**,* UP Chemical Co., Ltd., Republic of Korea

Aluminum nitride is a wide bandgap III-V compound with excellent thermal conductivity, high electrical resistivity, diffusion barrier properties, piezoelectric properties, and self-protection in oxidizing environments at high temperatures. It has been studied for various applications in electronics, optoelectronics, and microelectromechanical systems. Aluminum nitride thin films can be fabricated by physical vapor deposition, high-temperature chemical vapor deposition, and atomic layer deposition (ALD) techniques. ALD has several advantages including low process temperature, atomic-scale control of film thickness, and excellent step coverage on nanostructures. Aluminum chloride ($AlCl_3$), trimethylaluminum (TMA), tris(dimethylamido)aluminum (TDMAA), and tris(diethylamido)aluminum(TDEAA) were investigated as the aluminum precursor, and ammonia (NH_3) was used as the co-reactant. $AlCl_3$ is a solid and needs high deposition temperatures (≥500°C). Corrosive byproducts are also a concern. TMA exhibits a very narrow ALD temperature window near 350°C, below which the growth rate is very low due to poor reactivity of NH_3. Above that temperature, the TMA decomposes, resulting in the growth rate higher than monolayer growth. TDMAA and TDEAA have better reactivity with NH_3, but the thermal decomposition of the precursor limits the ALD temperatures to 250°C or lower, resulting in low film densities, low crystallinity, and high oxygen concentration [1]. In this work, we prepared high-quality ALD aluminum nitride films using a liquid aluminum dihydride complex and NH_3 at 300°C or higher temperatures. The deposited thin film had a composition in which the ratio of Al and N was 1: 1. Oxygen impurities were not detected by XPS after sputter etching of the surface layer. The ALD aluminum nitride of this work showed nearly 100% step coverage in the pattern with the aspect ratio of 10. The reaction of the precursor of this work with NH_3 or NH_2-terminated AlN surface was simulated by density functional theory (DFT) calculation and was compared with the reactions of other aluminum precursors.

References

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EM-MoP-9 Quinizarin: A Large Aromatic Molecule Ideal for Atomic Layer Deposition*, **Per-Anders Hansen**, O Nilsen,* University of Oslo, Norway

Atomic layer deposition is a remarkable synthesis tool due to the vast array of materials that can be deposited and the complexity of structures that can be designed. The low temperature layer-by-layer approach even allows organic and inorganic components to be combined as hybrid or composite materials. However, for organic and hybrid materials, it is challenging to find suitable precursors with large aromatic systems that are also can be sublimed and have necessary reactivity. This is a major barrier for using organic components for dye sensitized solar cells or luminescence, visible light photochemistry, chemical sensors and organic electronics with this technique.

In this work we introduce a well known orange dye molecule, quinizarin. This molecule has a large conjugated aromatic system with strong absorption of visible light and show strong luminescence both in solution and its resulting complex together with aluminium ions. Interestingly, quinizarin also show surprisingly good properties for film deposition due to reactive –OH groups and low sublimation temperature (130 °C). Strongly coloured pink hybrid films was deposited with trimethylaluminium and quinizarin at 175 °C with a growth rate of 0.76 nm/cycle with about 15 % thickness gradient for samples space 5 cm apart along the gas stream. The low sublimation temperature, good reactivity and large conjugated system of quinizarin opens up for explorations of solid state hybrid and organic films based on this molecule along many different technological paths.

EM-MoP-10 Superconducting and Insulating Nitride-Based Thin Films Deposited by Plasma Enhanced Atomic Layer Deposition*, I Gonzales Diaz-Palacio, L Ehmcke,* Universität Hamburg, Germany*; K Furlan,* Technische Universität Hamburg, Germany*; M Wenskat, W Hillert, R Blick, **Robert Zierold**,* Universität Hamburg, Germany

New concepts and materials for superconducting radio frequency (rf) systems have to be investigated to replace the bare niobium cavities, which are close to the theoretical performance limit nowadays. These novel approaches have the potential to further push the achievable accelerating fields and to reduce rf losses which in turn decrease operational costs or increase operational flexibility.

Here we report about thin film deposition of titanium nitride, niobium nitride, and mixtures of them by plasma enhanced atomic layer deposition from tetrakis(dimethylamino) titanium (TDMAT) and (t-butylimido)tris(diethylamino) niobium (TBTDEN) as metalorganic precursors. An adjustable ratio of nitrogen and hydrogen gas is used as co-reactant.

Structural and superconducting properties of the deposited thin films are characterized and optimized with respect to the deposition parameters, e.g. plasma power, plasma time, gas composition, and temperature. Specifically, in addition to the critical temperature and field, we reveal (i) a transition to an effective 2D electronic system and (ii) weak antilocalization in our titanium nitride films in low temperature magnetotransport studies proving the high quality and low impurity content.[1,2]

Furthermore, we compare the physical and structural properties of the superconducting thin films grown on insulating aluminum nitride, which has been deposited from trimethyl aluminum and a N_2/H_2-plasma without vacuum break, to oxygen- and hydroxyl group-terminated substrates such as Al_2O_3 or SiO_2 coated silicon wafers.

Our experimental studies lead to new insights in the ALD growth of superconducting nitrides and might be a stepping stone to ALD-deposited superconducting-insulator multilayer structures, which are treated as one of the most promising approaches to overcome the physical limitations of bare niobium cavities.

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[2] Gupta et al., *JMMM*, (2019) DOI: /10.1016/j.jmmm.2019.166094

EM-MoP-15 Low Temperature Thermal a-SiC Deposition Using Pulse CVD and ALD, ***Susumu Yamauchi***, *M Fujikawa,* Tokyo Electron Technology Solutions Limited, Japan*; T Miyahara,* TEL Technology Center, America, LLC

Semiconductor manufacturing processes are becoming increasingly complex and miniaturized year by year in order to achieve high performance, low power consumption and low manufacturing costs. From thin films point of view, this can be translated that thin films are required to be deposited at lower temperature, with high conformality and sometimes required to have high etch selectivity to other materials.

Despite enormous number of thermal SiO$_2$ and SiN deposition at low temperature < 450 ℃, not many thermal a-SiC deposition have been reported at low temperature. Most of SiC have been deposited at > 700 ℃ which might not be favorable to implement in manufacturing. On the other hand there are a lot of precedent reports of a-SiC deposition at low temperature which have done by plasma process. The authors agree with the usefulness of plasma enhanced deposition, but in the coming semiconductor manufacturing process with advanced scaling, there are concerns of conformality and plasma-induced damages.

Therefore, the authors have utilized thermal reaction without plasma enhancement to a-SiC thin film deposition (CVD, pulse-CVD and ALD) at low temperature. Several acetylene compounds have chosen as carbon precursor and disilane (Si$_2$H$_6$) has chosen as silicon precursor respectively. All of samples were deposited with CVD/ALD capable vacuum reactor. Precise process control has been established over wafer temperature, pressure and gas flow at every single process step. Detail physical characterization was carried out to study a-SiC film properties. Firstly, films were measured with SEM and ellipsometry to obtain thickness as well as deposition rate or growth per cycle (GPC). XPS measurement showed stoichiometry of deposited film and spectra were deconvoluted to analyze distribution of bond state as further research. EDX combined with TEM was also implemented to some of samples. Film density was measured with XRR. In-film hydrogen concentration was measured by HFS. Conformality of deposited film was inspected with TEM and SEM.

Thermal a-SiC was successfully deposited at ≥ 400 ℃. Typical deposition rate or GPC of pulsed CVD and ALD were 0.60 Å/cyc and 0.32 Å/cyc respectively. Film stoichiometry were Si/C/O = 51/47/2% with pulse-CVD and Si/C/O = 49/44/7% with ALD respectively. XPS peaks deconvolution for both Si2p and C1s indicated that ≥ 80% of silicon and carbon formed Si-C bond. Film density was ~ 2.3 g/cm^3. Step coverage of film was confirmed with A/R = 1:3 to 1:7 trenches and which showed good conformailty. Dry etch rate was 8.2 to SiO$_2$ and 7.8 to SiN respectively.

EM-MoP-16 Novel Approach for Conformal Chemical Vapor Phase Deposition of Ultra-Thin Conductive Silver Films, ***Sabrina Wack***, *P Lunca Popa, N Adjeroud, R Leturcq,* Luxembourg Institute of Science and Technology, Luxembourg

The present work demonstrates a novel approach for the conformal deposition of ultra-thin conductive silver (Ag) films on complex substrates. Using an original multi-step plasma-enhanced approach, we demonstrate the deposition of conductive silver films with thickness down to 11 nm. Conductive ultra-thin Ag films are commonly deposited by physical vapor deposition techniques (metal evaporation or sputtering). However, these are line-of-sight methods that do not allow conformal deposition on substrate with complex morphology (e.g. trenches) [1]. Non line-of-sight methods such as the ones based on chemical vapor phase deposition (Chemical Vapor Deposition-CVD or Atomic Layer Deposition-ALD) usually produce non-electrically-conductive films for thickness below 20-50 nm due to island formation by Volmer-Weber growth mode for metal layers on oxide-based substrate [2]. Moreover, conductive ultra-thin silver films based on ALD (down to 22 nm) [3], require low-temperature deposition (below 120 ºC), with a very narrow process temperature window (about 10 ºC).

The deposition is based on Ag(fod)(PEt$_3$) as silver precursor, and H$_2$ plasma as reducing agent. An acceptable process temperature window (> 30 ºC), and a deposition temperature larger than 120ºC for enhanced uniformity and deposition rate have been demonstrated. In these conditions, highly uniform deposition on bent and batched samples have been performed. 20 nm thick films exhibit a resistivity down to 40 μΩ·cm. The resistivity increases up to 1.4 mΩ·cm when reducing the thickness down to 11 nm. The critical thickness as low as 11 nm is thus very close to the state-of-the-art for sputter-deposited thin films [4], and well below the 22 nm obtained with ALD [3]. The obtained Ag thin film also demonstrates a high reflectance up to 94% and a low absorbance of 3% in the infrared region for a film thickness of 36 nm, showing the high quality of the films. This quality is confirmed by morphological analysis using scanning electron microscopy and atomic force microscopy, as well as by the structural (X-ray diffraction) and chemical (energy dispersive X-ray spectroscopy) properties. This new processing approach opens a very interesting path for the use of ultra-thin silver films for electronic and optoelectronic applications.

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[2] Golrokhi *et al.*, Applied Surface Science, 364, 789–797 (2016)

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EM-MoP-17 When ALD Outperforms MOCVD: Direct Comparison of Epitaxial InN Films, ***Chih-Wei Hsu***, *P Deminskyi, I Martinovic, J Palisaitis, H Pedersen,* Linköping University, Sweden

The successful development of III-nitride semiconductors and their alloys for light-emitting and power electronics has attracted tremendous attention over the past few decades. InN, with direct band gap of 0.7 eV and high carrier mobility, has been suggested to play a key role in extending the LED toward infrared and lifting the operating frequency of a high-electron-mobility transistor. However, the utilization of InN in device structures is rare due to the challenges of integrating high quality InN as active layers in between other matrix material.

In this work, homogeneous and epitaxial InN layers with well-controlled thickness grown on GaN and SiC by using plasma ALD is presented and compared to InN grown by conventional Metal-Organic Chemical Vapor Deposition (MOCVD). Trimethyl indium and NH$_3$ are used as precursors in both plasma ALD and MOCVD with the main difference of it being supplied in a plasma discharge in the case of plasma ALD. The morphological and structural properties of the resulting materials are characterized by using scanning electron microscopy, atomic force microscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The surface profiles and the surface roughness of InN grown by ALD are nearly identical to those of GaN and SiC. In contrast, scattered hill-rock features are observed on InN grown by MOCVD. Despite the difference in morphology, the InN grown by ALD and MOCVD have the same hexagonal wurtzite structure and is epitaxially grown on GaN and 4H-SiC with the growth direction of <0002>. The full-width-half-maximum of XRD rocking curve of InN (0002) is well-reproduced depending on the quality of underlying material; the measured values for our ALD grown InN (0002) are between 150-200 arcsecond for InN on GaN and between 20-30 arc seconds for InN on 4H-SiC. This result is better than any other reported value for InN (0002) rocking curves. The observation of interference fringes in the vicinity of InN (0002) suggests very smooth InN layer with sharp interface grown by ALD. Such features are absent in InN grown by MOCVD. The well-resolved lattice images obtained in our TEM investigation further confirm the epitaxial relationship between InN and its underlying materials.

In summary, the InN grown by ALD results in smooth and homogeneous films with good crystalline quality while the InN grown by MOCVD results in hill-rock structures after relaxation. Our results suggest that ALD is a promising growth technique that can enable the use of InN layer in optoelectronic applications.

EM-MoP-19 Solution-Based ALD Routes Towards Thin Films of Organic-Inorganic Hybrid Perovskites, ***Vanessa Koch***, *M Barr, P Büttner, I Mínguez-Bacho, D Döhler, J Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany

Organic-inorganic hybrid perovskites are not yet accessible with conventional Atomic Layer Deposition from the gas-phase (gALD). Therefore, a method to deposit such materials in a precise and controllable manner is necessary. We present two procedures to grow organic-inorganic hybrid perovskite thin films with 'solution Atomic Layer Deposition' (sALD), a technique which transfers the principles of ALD from the gas phase to liquid processing at ambient conditions. The first route entails two steps: the successful deposition of polycrystalline PbS thin films on planar and nanostructured substrates *via* sALD with subsequent conversion to the hybrid perovskite methylammonium iodoplumbate (methylammonium lead iodide, MAPI, CH$_3$NH$_3$PbI$_3$). The second route paths the way to a direct deposition of hybrid perovskites including lead-free phases. These materials can then serve as light-absorbing layers in thin film solar cells.

EM-MoP-21 Development of ALD Copper Oxide and Al:Cu$_x$O Films, *J Avila, C Eddy, Jr.,* ***Virginia Wheeler***, U.S. Naval Research Laboratory

Thin film metal oxide semiconductors that exhibit p-type conductivity are advantageous for a wide variety of applications, such as photovoltaics and high power electronics. Copper containing materials, like Cu_2O and $CuAlO_2$, are promising p-type oxides due to O-Cu-O structure facilitating hole carriers through copper vacancies.[1,2] Additionally, the wide bandgap of $CuAlO_2$ (3.5 eV) results in ~70% transparency of visible light[1], which is useful for transparent conductors. ALD of Cu_2O or $CuAlO_2$ would allow conformal thin films on a variety of substrate materials and complex architectures required for many new applications. There are few studies demonstrating the growth of either Cu_2Oor $CuAlO_2$ by ALD,[2] and even fewer showing the systematic effect of digitally doping of Cu_2O films with increasing amounts of Al on film quality. In this work, the chemical, structural, and electrical properties of ALD grown Al:CuO films will be assessed as a function of increasing amounts of Al.

Due to its relatively high growth rate, deposited crystallinity,[3] and stoichiometric modularity, Bis(dimethylamino-2-propoxy)copper(II) (or Cudmap) was used with ozone to deposit CuO films at 150°C CuO films were digitally doped with individual Al_2O_3-cycles using trimethylaluminum (TMA) and ozone. The ratio of Al_2O_3 to CuO cycles was varied from 2-50 cy%. Initial films indicate that only 2 cy% of Al is needed to reach stoichiometric 1:1 ratio with Cu, and dramatically changes the properties of the film resulting in increased growth rate and reduced film crystallinity. Furthermore, XPS analysis of a 50 cy% films, indicates that TMA reduces the CuO film to a mixed Cu--$^{+}$/Cu^{2+} oxidation state.

The influence of crystallinity on the electrical properties of Al:CuO films was studied through post-deposition annealing. Initially, CuO films were annealed to determine the parameters required to crystallize and reduce CuO to Cu_2O, the necessary stoichiometry for $CuAlO_2$ films. Oxygen pressure was crucial to attaining continuous films with the required crystalline structure and phase, while temperature and time were less impactful. Specifically, a low pressure of 0.1 mTorr of O_2 is required to achieve crystalline Cu_2O from the as-deposited CuO ALD film. Using the established optimized annealing conditions, the effect of Al incorporation on the final film crystallinity, morphology and electrical properties was assessed as a means towards realizing usable p-type oxide films for optoelectronic devices.

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EM-MoP-23 Photoactive Hybrid Thin Films by Molecular Layer Deposition

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Photoreactive surfaces can be utilized in solar cells, light sensors and photocatalytic processes for water purification systems or antimicrobial coatings. One of the promising method to design such photoactive materials is to extend the light absorption towards the visible light region by combining inorganic transition metal clusters with highly aromatic organic molecules. Molecular layer deposition (MLD) is a suitable tool to fabricate such structures with an excellent thickness control.

In this study we have produced organic-inorganic hybrid materials with photoactive properties based on 2,6-naphthalenedicarboxylic acid as the absorber and organic building unit, and Ti, Zr, Hf or Y as metal centre. We characterized the growth dynamics and physicochemical properties of our surfaces with in-situ QCM, FTIR, UV-Vis and photoluminescence (PL) measurements. The films are amorphous as deposited and prove strong photoactivity and photoluminescence. The growth dynamics

is dependent on the choice of a metal and our current focus is in identifying the effect of chemistry on the growth and material properties.

In all deposited systems, the strong near-UV absorption of the organic precursor is broadened and

red-shifted when the organic molecule binds to a metal atom. The PL characterization proves that the presence of different metal clusters change the optical emission of hybrid systems and moreover

Ti-O clusters quench the emission from the organic linker. It was also found that the emission of light from the photoactive materials decreases upon UVC exposure, showing photobleaching effect.

EM-MoP-24 Inducing Conductivity into Parylene C by Vapor Phase Infiltration of In_2O_3

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The development of material for future electronics does not only rely on increasing the computational efficiency, but also on including completely novel functionalities, such as foldability. Hybrid organic-inorganic materials are especially promising for this task as they may combine the properties of inorganics, such as electronic conductivity, with the flexibility of organic polymers.

A hybrid system, consisting of a semiconducting material blended with a polymer matrix, may be beneficial over conventional approaches that rely on coatings and well-defined interfaces between the two materials. Vapor phase infiltration (VPI) meets this challenge by allowing diffusion of a precursor into the bulk of a soft substrate. VPI on polymer substrates leads to the formation of a gradient hybrid layer with altering density and smooth transition from the bulk polymer to the inorganic thin film on the surface (Fig.1). This gradient layer can compensate mechanical stress and suppress crack formation upon bending, thus preventing the loss of electrical conductivity upon bending, folding, or stretching.

In this work, we developed a VPI process of indium oxide by exposure of parylene C to alternating pulses of trimethylindium and water precursors. Parylene C is a CVD-deposited polymer with high thermal tolerance. The infiltration process was performed in the temperature range from 130 to 210^{o}C. Despite the film growth even at low temperatures, the sheet resistance of those structures remained high at 130^{o}C. Substitution of the water with hydrogen peroxide allowed to decrease the sheet resistance value by five orders of magnitude and highlighted the importance of the oxygen source choice. For higher infiltration temperatures this difference decreased to one order of magnitude for water and H_2O_2 precursors. However, the precursor choice made a significant impact on the infiltration depth, chemical distribution of the elements, and crystallinity. Moreover, transmission electron microscopy showed that in the case of hydrogen peroxide, there is no thin inorganic film growing on top of the surface, but the whole surface remained hybrid. Such functionalization of the dielectric polymer with electronically conductive material is a promising approach for the development of novel foldable organic electronic devices.

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EM-MoP-26 Solution Atomic Layer Deposition of Cu-BDC SURMOF Thin Films

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Transferring the principles of atomic layer deposition (ALD), known with gaseous precursors, to precursors dissolved in a liquid generalizes established methods such as the 'layer by layer' growth or the 'successive ion layer adsorption and reaction' (SILAR). This 'solution ALD' (sALD) shares the fundamental properties of standard 'gas ALD' (gALD), especially the self-limiting growth and the ability to coat deep pores.

It is particularly interesting in the case of ionic solid or polymers. In the specific case of metal-organic fameworks (MOF), the use of sALD appears as a method of choice. Indeed the usual processes such as spray coating, spin coating and dip coating do not offer a control at the scale of individual units (molecules or ions). So far, only few processes from the gas phase, including ALD, have been reported due to the competition of the growth and the thermal decomposition of the MOF at elevated temperature under vacuum.

In the following the deposition of a surface-anchored metal-organic framework (SURMOF) is described. The optimization of the deposition conditions is studied for the growth of Cu-BDC by sALD. Copper acetate and benzene-1,4-dicarboxylic acid (BDC) are used as the copper source and the linker, respectively. The purge and pulse durations are varied independently and demonstrate the self-limiting feature of this sALD reaction. The morphology of the films is observed by scanning electron microscopy and atomic force microscopy. The films are crystalline MOF is identified by x-ray diffraction and TOF-SIMS. The thin SURMOF films obtained by sALD exhibit a quality superior to layers obtained by spray and dip coating: in particular, the films are continuous and uniform after only 10 cycles already.

EM-MoP-29 ALD-Grown Gallium Oxide Thin Films with Properties Close to Bulk Wafers

Elham Rafie Borujeny*, K Cadien,* University of Alberta, Canada

Gallium oxide is a wide bandgap material (Eg ~ 4.6eV - 5.2eV) with a large breakdown field (~ 8MV/cm). These properties make gallium oxide a promising material for power semiconductor applications [1]. A comprehensive study of gallium oxide thin films grown by ALD is presented in this work, and ~40nm-thin films with properties close to bulk gallium oxide wafers are obtained.

Gallium oxide films were deposited on C-plane sapphire, p-Si (100), n-Si (111) and p-Si (110) wafers as well as glass slides using a Kurt J. Lesker ALD 150-LX™ system equipped with a remote inductively coupled plasma (ICP) source. Depositions were done at a substrate temperature range of 50°C to 450°C. In-situ ellipsometry measurements were performed and the results were used to predict the quality of the films at different deposition conditions. 1-D and 2-D XRD patterns were collected to study crystallinity of the films. AFM measurements were performed to study surface morphology of the films. Electrical resistivity of the films was measured using van der Pauw method. Characterization results confirmed robustness of ellipsometry as a fast, non-contact and non-destructive technique for predicting structure and property of the films, which is especially beneficial for highly resistive thin films of emerging wide bandgap materials such as gallium oxide.

As a result of this work, low temperature gallium oxide thin films with resistivity and breakdown voltage values close to bulk wafers have been successfully deposited by ALD. An example cross section TEM image of a film grown at 275°C is shown in the attachment to present the crystalline quality of the film both at the interface and throughout the bulk of the film.

References:

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EM-MoP-30 Crystalline GaN Film Growth at a Thermal Budget Approaching 100^{o}C Using Hollow-Cathode Plasma-Assisted Atomic Layer Deposition*, **Deepa Shukla**, A Mohammad, S Ilhom, N Biyikli,* University of Connecticut

The III-nitride wide bandgap semiconductor material family features attractive properties to be integrated with low-temperature materials such as transparent glass and polymeric flexible substrates. Towards such an integration, our plasma-assisted atomic layer deposition (PA-ALD) efforts concentrated on achieving a minimal deposition thermal budget not exceeding 200 ^{o}C. Our previous efforts demonstrated the effectiveness of the hollow-cathode plasma source in obtaining relatively low-impurity GaN layers at a substrate temperature of 200 ^{o}C. Using our customized hollow-cathode PA-ALD (HCPA-ALD) reactor, in this work, we achieved crystalline hexagonal GaN films at growth temperatures as low as 120 ^{o}C. To the best of our knowledge, this corresponds to the lowest growth temperature for crystalline GaN films via remote-plasma ALD.

GaN thin films were successfully deposited using HCPA-ALD on Si(100) substrates using triethylgallium (TEG) and Ar/N_2/H_2 or N_2/H_2 plasma as metal precursor and nitrogen co-reactant, respectively. Saturation curve study revealed an optimal plasma power of 150W and plasma duration of 20 s. The temperature range for the saturation experiments was 100 – 240 °C and each growth parameter variation was carried out for 10-cycle sub-runs. The sensitivity of the multi-wavelength *in-situ* ellipsometer has provided sufficient resolution to capture the subtle changes in the growth-per-cycle (GPC) parameter. The temperature variation of the GPC demonstrates a slight increase with temperature till 200 ^{o}C, where after it reaches a plateau, indicating a possible ALD temperature window for the TEG-N_2/H_2 surface growth reaction. Structural, chemical, and optical characterizations were performed to evaluate and compare film quality of GaN films grown at different substrate temperatures. The influence of plasma gas composition on film crystallinity has been characterized using grazing-incidence x-ray diffraction (GIXRD) and it was observed that the absence of Ar plasma during the growth process enhances the preferred (002) crystalline orientation by suppressing (100) & (001) neighbor peaks. In addition, we found that the optimal N_2/H_2 flow ratio is 1:2, reaching the highest (002) peak intensity. High-resolution XPS measurements revealed near-ideal stoichiometry with relatively low oxygen incorporation and below-deteccarbon content lower than the XPS-detection limits. High-resolution TEM imaging confirms the polycrystalline structure along with the crystal planes within the film grown at 120 ^{o}C. A detailed analysis comparing previously published reports on PA-ALD grown GaN will be presented.

Emerging Materials
Room Jan & Hubert Van Eyck - Session EM-WeM

Organic and Organic-Inorganic Hybrid Materials I

Moderators: Steven M. George, University of Colorado at Boulder, Mato Knez, CIC nanoGUNE

11:00am **EM-WeM-2 Vapor-Phase Synthesis and Surface Area Analysis of ZIF-8 Metal Organic Framework (MOF) on Fibrous Substrates via Atomic Layer Deposition***, R Nye, S Smith,* ***Nicholas M. Carroll****, G Parsons,* North Carolina State University

Solvent-free synthesis methods for metal-organic frameworks (MOFs) will help expand their applications in catalysts, gas adsorption, and sensors. Unfortunately, methods of using atomic layer deposition on silicon wafers to convert a metal oxide to MOF prevent surface area measurements, which are critical in the aforementioned applications. In this work, we describe low-temperature formation of zeolitic imidazolate framework (ZIF-8) MOF on high-surface area polypropylene polymer fiber substrates via vapor-directed conversion of ALD ZnO. The resulting MOF-fiber structures are highly stable and withstand robust mechanical deformation, demonstrating excellent MOF adhesion to the polymer fiber surface. Moreover, for the first time, our synthesis approach enables direct gas adsorption analysis of vapor-derived MOFs, including determination of net surface area by Brunauer-Emmett-Teller (BET) analysis. To form the MOF-fiber structure, approximately 10 nm of zinc oxide is deposited at 90°C via ALD on nonwoven polypropylene fiber mats. The coated mats are then placed into a loosely sealed vessel containing 2-methylimidazole powder and heated at 100-135 C for 1-24 hours, enabling volatilization of the 2-methylimidazole and reaction with the solid ZnO to form ZIF-8 crystals. During the process, the pressure in the vessel is maintained at atmospheric pressure. The formation of ZIF-8 is confirmed by XRD, and SEM shows crystals of ~100-300 nm on the fiber surface. BET analysis on the MOF-coated fiber mats demonstrated surface area values of 400 m^2/g (fiber+MOF). Using the mass of MOF determined by sample weight before and after MOF growth, the surface area of the ZIF-8 on the fibers in 1500 m^2/g ZIF-8, which is comparable to ~1300 m^2/g expected for ZIF-8 powder, indicating good quality of synthesized MOF. To the best of our knowledge, this is the first report of surface area measurements on solvent-free MOFs. By tuning deposition and conversion parameters, the crystallinity and surface area of the ZIF-8 can be controlled. This MOF formation on fibers enables applications and measurements not otherwise available, such as incorporation into protective garments. Additionally, successful vapor-phase MOF synthesis opens the doors for selective deposition of MOFs for use in sensing and electronic applications.

11:30am **EM-WeM-4 Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Mechanisms of Inorganic Entrapment and Structure-Property Implications***,* ***Mark Losego****,* Georgia Institute of Technology **INVITED**

Vapor phase infiltration (VPI) transforms polymers into organic-inorganic hybrid materials by infusing the polymer with inorganic constituents from the gas phase. Hybrid materials synthesized with VPI have been demonstrated for numerous applications ranging from energy harvesting to filtration media to photolithographic hard masks. The infiltration process consists of three basic steps: (1) sorption of the gaseous precursor molecule into the polymer, (2) diffusion of the precursor throughout the polymer, and (3) “entrapment” of that precursor within the polymer. This talk will focus on this final step: “entrapment”. The mechanism of entrapment informs both how to design an infiltration process and the final chemical structure of the hybrid material. Processes for entrapment can largely be understood by the energy landscape for precursor binding and reaction with the polymer. Most important to understand is the depth of the energy well for the bound state and the activation energy for the reaction pathway. These energetics determine whether a precursor is easily entrapped and whether the final hybrid has unbound or chemically bound inorganic constituents. In this talk, we will show evidence from our lab for infiltrated materials where the inorganic constituents are homogeneously distributed throughout the hybrid material but are chemically unbound to the organic – creating an interpenetrating, unbound organic-inorganic bicontinuous network. Similarly, we will show how increasing reaction temperature can increase the probability for chemical reactions and covalent bond formation. Subsequently, we will show how these different chemical states lead to differences in material properties including solubility, glass transition, thermal expansion, and interfacial adhesion strength.

Emerging Materials
Room Jan & Hubert Van Eyck - Session EM-WeA
Organic and Organic-Inorganic Hybrid Materials II & III

Moderators: Tero Pilvi, Picosun Oy, Ganesh Sundaram, Veeco-CNT

1:15pm **EM-WeA-2 Enhanced Stretchability in Inorganic-Organic Alucone Thin Films Deposited from Long-Chain Organic Precursors***, **Janne-Petteri Niemelä**, N Rohbeck, J Michler, I Utke,* Empa, Switzerland

Molecular layer deposited (MLD) hybrid inorganic-organic materials ("metalcones") have recently received increasing attention, largely due to their potential for applications demanding mechanical stretchability/flexibility.[1,2] Alucones (Al-based hybrids) are among the most studied metalcones owing to e.g. their promising performance as an electrode-electrolyte interface layer in Si-nanoparticle based batteries, where the charging/discharging cycles involve huge volumetric changes up to 300 %.[3] The research on mechanical (and battery) properties of metalcones is limited to the materials based on short-chain organic precursors,[4] while increasing the precursor chain length is an unexplored but rational route for enhancing mechanical performance of the metalcone thin films.

In this work we deposited alucone thin films using trimethyl aluminum (TMA) as the Al metal precursor, and 1,2-ethanediol (EG), 1,6-hexanediol (HD) and 1,10-decanediol (DD) as the organic precursors. The TMA/HD and TMA/DD processes were studied at 130 °C: they exhibit MLD-type behavior with self-saturating surface reactions, and linear film growth (studied up to 150-200 nm) with the growth-per-cycle values of 0.32 and 0.37 nm, respectively. Mechanical stretchability was studied via tensile testing coupled with in-situ optical microscopy for 100-nm alucone films deposited on the stretchable polyimide substrates. The critical strain for fracture was enhanced up to around 9 % for the alucone films deposited via the TMA/DD process. This value is more than an order-of-magnitude higher than the value for purely inorganic Al_2O_3 and represents a factor-of-four increase in comparison to the EG-based alucone material (the state-of-the-art for the metalcones). The 9-% critical strain translates to critical volume expansion of 300 % for (battery-relevant)[3] around 3-nm coating thickness on a nanoparticle surface (assuming a spherical particle and inverse-square-root thickness extrapolation for the critical strain), and to 0.25-mm critical bending radius on the 50-µm substrate. The film structure is moreover studied via the XRR, FTIR and SEM techniques, while the mechanical properties are further analyzed via nanoindentation.

The present results highlight that the potential of the MLD technique can be further enhanced by exploring a wider space of larger/longer/complex organic precursor molecules instead of the conventionally used small molecules.

(1) X. Meng, J. Mater. Chem. A, 2017, 5, 18326.; (2) J.-P. Niemelä et al., J. Mater. Chem. C, 2015, 3, 10349. (3) D. M. Piper, et al., Nano Energy, 2016 22, 202. (4) M. Ruoho, I. Utke et al., Mater. Today Chem. 10 (2018) 187.

1:45pm **EM-WeA-4 Self-Terminating Molecular Layer Deposition of Polyurea and Growth Rejuvenation via Precursor Linking Group Selection***, **Rachel A. Nye**, G Parsons,* North Carolina State University

Molecular layer deposition (MLD) has recently been explored due to the vast tunability of film properties and growth conditions. Polyurea coupling by MLD commonly proceeds by reacting molecules with diisocyanate functional groups (such as p-phenylene diisocyanate, PDIC) with other molecules containing diamine functional groups (such as ethylenediamine, ED). Under steady-growth conditions at 60°C, the PDIC/ED sequence typically leads to continuous film growth of ~0.41 nm/cycle. Recently, we discovered a modified polyurea MLD reaction that shows a growth trend very different from commonly reported processes. Specifically, we find that using 1,6-hexanediisocyanate, HDIC, in place of PDIC, causes a significantly lower film growth rate: less than 0.1 nm/cycle even at temperatures as low as 40°C.

Additionally, the low growth rate obtained from the HDIC/ED reaction continues to decrease with increasing cycle number. This significant change in polyurea growth rate is achieved simply by varying the organic linker groups, while maintaining the same urea coupling chemistry. Interestingly, the low growth rate of the flexible HDIC/ED can be increased by incorporating the aromatic PDIC compound into the overall polymer structure. Thus, the self-terminating and rejuvenating growth of aliphatic polyurea can be controlled with aromatic composition. The entirely flexible HDIC/ED polymer is very difficult to grow to a thick film, but incorporating small amounts of benzene enable deposition of a much thicker film without significantly affecting film properties. These trends are likely due to high frequency of double reactions for the entirely aliphatic HDIC and ED precursors. The rigid benzene ring in the PDIC precursor then seems to promote a more rigid structure that reduces the number of site-terminating reactions and enhances growth. This self-limiting and rejuvenating growth is of potential interest for the field of area selective deposition. Additionally, the ability to modulate polymer growth rates with the incorporation of benzene rings has significant implications to the development of new precursors and polymer thin film properties.

3:00pm **EM-WeA-9 Vapor-Phase Infiltration Synthesis of Organic-Inorganic Hybrid Nanocomposite Resists for Next-Generation Nanolithography***, N Tiwale,* Brookhaven National Laboratory*; A Subramanian,* Stony Brook University*; K Kisslinger, G Freychet, M Lu,* Brookhaven National Laboratory*; J Kim,* University of Texas at Dallas*; A Stein, **Chang-Yong Nam**,* Brookhaven National Laboratory

Vapor-phase infiltration (VPI), a material hybridization technique derived from atomic layer deposition, can generate molecular-scale organic-inorganic nanocomposites with uniquely enhanced material properties by utilizing the infiltration and binding of gaseous organometallic precursors within organic media. In this study, we report the application of VPI on developing new organic-inorganic hybrid polymer resists for the next-generation nanolithography. Hybrid resists are emerging as an effective way of addressing stringent process requirements for aggressive down-scaling of semiconducting devices. However, hybrid resists generally require complex chemical synthesis while being predominantly negative-tone with high exposure dose requirement. For positive-tone processes and high-aspect-ratio pattern transfer, resist choices are limited to costly non-hybrid alternatives, whose etch resistance is still inferior compared with hybrid resists. Here, demonstrated is a novel hybrid positive-tone resist platform utilizing simple *ex-situ* VPI of inorganic components into standard resist materials. A model system based on poly(methyl methacrylate) (PMMA) thin film hybridized with AlO_x has been demonstrated for electron-beam lithography patterning, featuring fully controllable critical exposure dose, contrast, and etch resistance. The hybrid resist not only achieves exposure contrast as high as ~30, a six-fold enhancement over standard PMMA, but also enables Si nanostructures with resolution down to ~30 nm and aspect ratio up to ~17, owing to extremely high Si etch selectivity far exceeding those in known commercial positive-tone resist systems. Interrogation of the effect of varying etching protocols on etch rate reveals a surprisingly high enhancement of chemical etch resistance over the physical one with increasing amount of infiltration, which we attribute to the strong chemical biding between infiltrating Al precursor, trimethylaluminum (TMA), and carbonyl group in PMMA. Also briefly discussed is the electron-beam-induced exposure mechanism (i.e., change in solubility) in the hybrid resist probed by synchrotron X-ray absorption spectroscopy as well as other hybrid resist systems being developed for extreme ultraviolet (EUV) lithography application, where the infiltrated inorganic elements can potentially improve not the etch resistance but also EUV sensitivity and other resist performance parameters. The easy implementabilility, combined with versatile *ex-situ* control of resist characteristics, makes this hybrid resist synthesis approach uniquely suited for addressing the resist performance required for advanced next-generation nanolithography techniques.

3:45pm **EM-WeA-12 Synthesis of SiAlCO Polymer Derived Ceramics (PDC) Thin Films using Molecular Layer Deposition***, **Kristina Ashurbekova**,* Dagestan State University, Russian Federation*; E Modin, A Chuvilin, M Knez,* CIC nanoGUNE BRTA, Spain*; I Abdulagatov,* Dagestan State University, Russian Federation

Organosilicon PDC materials and its derivatives have gained interest for various important applications such as electrode material for lithium-ion batteries, ultra-high temperature composites and others [1]. Conventionally, PDC coatings are prepared by wet-chemical dip, spin, thermal-spray coating or by plasma-assisted chemical vapor deposition (CVD), followed by high temperature pyrolysis [2].

In this work, molecular layer deposited (MLD) hybrid organic-inorganic films serve as precursors for a synthesis of SiAlCO PDC composite coatings. Alumina-polysiloxane films were grown using 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4D_4) and trimethylaluminum (TMA) (Supplemental Figure 1). The deposition was conducted at temperatures between 120 and 220°C. An *in-situ* quartz crystal microbalance (QCM) study showed linear mass increase with the number of MLD cycles with the highest growth rate of 24 ng/cm^2/cycle occurring at 180^{o}C. QCM measurements revealed a self-limiting surface chemistry of the MLD process. FTIR analysis of deposited films showed vibrational features characteristic of organosilicon polymers: Si-CH$_3$, Si-O-Si, Si-CH=CH$_2$ and Si-O-Al peaks (Supplemental Figure 2).

Upon growth of the film, cross-linking is needed to increase the mass yield during the polymer-to-ceramic transformation. Cross-linking was achieved at 200^{o}C by introducing a third precursor, di-tert-butyl peroxide (TBP), into the MLD process, following a V$_4$D$_4$/TBP/TMA sequence. The thus obtained films were pyrolyzed at 900^{o}C in an Ar atmosphere. XRR, XRD, Raman, HRTEM, and EDX were applied for characterization of the films. After pyrolysis, the composite thin film remained amorphous. The final film contained Si, Al, O, and C uniformly distributed throughout the film. Raman spectroscopy showed presence of graphitic carbon within the film. This MLD-derived SiAlCO thin film is expected to have exceptional high temperature stability, creep, and corrosion resistance.

[1] P. Colombo, et al., *J. Am. Ceram. Soc.,***93** (7), 1805–1837 (2010)

[2] G. Borroso, et al, *J. Mater . Chem. A.,* **7**(5), 1936–1963 (2019)

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