Emerging Materials
Room Evergreen Ballroom & Foyer - Session EM-MoP
Emerging Materials Poster Session

EM-MoP-1 Structure and Magnetism of Electrospun a -Fe_2O_3 Nanofibers SiO_2-Coated by ALD*, F Pantò,* CNR-Istituto di Tecnologie Avanzate per l'Energia (ITAE), Italy*; H Raza,* Humboldt-Universität zu Berlin, Germany*; A Ferretti,* CNR-Istituto di Scienze e Tecnologie Molecolari (ISTM), Italy*; C Triolo,* Università di Messina, Italy*; A Ponti,* CNR-Istituto di Scienze e Tecnologie Molecolari, Italy*; S Patanè,* Università di Messina, Italy*; N Pinna,* Humboldt-Universität zu Berlin, Germany*; **Saveria Santangelo,*** Università Mediterranea, Italy

In the last years, thanks to its appealing properties (high abundance, low-cost, environmental friendliness, good chemical stability, small energy band gap) hematite has attracted considerable attention as a photocatalyst for the H_2 production. Electrospun α-Fe_2O_3 nanofibers (NFs) have been evaluated in other energy related applications potentially benefiting from their high porosity and large surface area and could also be utilized in less common ones, e.g., as a theranostic agent [1]). Besides, magnetism of nanohematite is a current topic in fundamental research. [2] A study focused on the magnetic properties of electrospun α-Fe_2O_3 NFs has shown that the fiber diameter strongly controls the magnetic behaviour [3]. Coating elongated α-Fe_2O_3 nanoparticles (NPs) by silica via sol-gel chemistry allows controlling the saturation magnetisation, remanent magnetisation and coercivity through the thickness of the coating layer [4]. ALD offers the possibility to coat NPs with well-calibrated and conformal thin films, thus in principle enabling the fine-tuning of the magnetic properties. This contribution focuses on SiO_2-coated electrospun a-Fe_2O_3 NFs and their nanostructure. The changes of the magnetic properties, with respect to pristine hematite, due to the SiO_2 coating are discussed as a function of the number of ALD cycles (10–100) and of the sequence of the production steps (i.e. calcination of the electrospun NFs followed by SiO_2-ALD or vice versa). SiO_2-ALD prior to calcination results in fibers formed by smaller α-Fe_2O_3 grains and by a higher structural disorder. Regardless of the sequence of production steps, ALD coating brings about a local rearrangement process in the oxide lattice with gradual surface defects suppression. These structural changes reflect on the magnetic NF properties, especially coercivity and remanence (Morin temperature).

[1] Chem. Mater. 26 (2014) 2105

[2] J. Magn. Magn. Mater. 475 (2019) 611

[3] J. Phys. Chem. C 115 (2011) 17643

[4] *Mater. Lett. 61 (2007) 5268*

EM-MoP-2 Fluidized Bed Molecular Layer Deposition of Ultrathin Poly(ethylene terephthalate) Films on TiO_2 P25 Nanoparticles*, **Damiano La Zara**, M Bailey, D Benz,* Delft University of Technology, Netherlands*; M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden*; J van Ommen,* Delft University of Technology, Netherlands

Molecular layer deposition (MLD) is a vapour phase technique allowing the controlled, layer by layer growth of purely organic thin films on a wide range of substrates. To date, most MLD studies have focused on coating flat substrates, but MLD also holds significant promise for application to particles. In particular, the inherent biocompatibility of organic coatings is of interest to passivate the surface of pigment particles and to tailor the dissolution profile of drug particles. Of the organic coatings produced thus far, polyimide and polyurea coatings predominate, whereas polyester polymerisation chemistry has received considerably less attention. Amongst this class of polymers, Poly(ethylene terephthalate) (PET) is of particular interest due to its widespread industrial usage, thermal stability, and gas and moisture barrier properties stemming from the terephthalate group. The use of conventional deposition reactors operating at vacuum conditions, reported in nearly the entirety of MLD literature, hinders facile and low cost up-scaling. Therefore, the development of processes with better scale-up potential is crucial when aiming for commercial applications, especially when it concerns high-surface area powders.

In this work, we deposit ultrathin PET films on gram-scale batches of TiO_2 P25 nanoparticles (NPs) using terephthaloyl chloride and ethylene glycol as precursors. The MLD process is carried out in an atmospheric-pressure fluidized bed reactor at 150-160 °C for a broad range of growth cycles (i.e., from 5 to 50). Ex-situ diffuse reflectance infrared fourier transform spectroscopy (DRIFTS-FTIR) shows the presence of the characteristic C=O stretch of ester groups in the range 1730-1750 cm^{-1}, thus demonstrating the successful MLD reaction. DRIFTS-FTIR and thermogravimetric analysis (TGA) confirm the self-saturating behaviour of the precursors, and the linear increase in mass with the number of cycles. Moreover, TGA highlights the good thermal stability of the PET films, which are stable up to ~225 °C. Transmission electron microscopy (TEM) enables the visualization of uniform PET films on the surface of TiO_2 NPs. Preliminary TEM observations suggest a low PET growth per cycle (GPC), around 0.03-0.04 nm. This value seems also in agreement with the GPC estimated by the amount of deposited material on TiO_2 NPs measured by TGA as well as with the GPC of PET on SiO_2 wafers measured by spectroscopic ellipsometry. Finally, ultrathin PET films are effective in suppressing the photocatalytic activity of the TiO_2 P25 NPs, without affecting its absorptive properties in the UV-vis spectrum.

EM-MoP-3 Fabrication and Characterization of Organic-Inorganic Hybrid Thin Films*, S Mo, **Chu Huong,*** Hanyang University, Republic of Korea

Currently, the next generation of electronic devices requires new materials that have great properties. The straight way to fabricate new materials is the hybridization of existing materials having different properties. The hybrid materials mixed by organic and inorganic components are expected to have combined properties both of inorganic parts, such as stability and high electrical or optical performance and organic parts with great flexibility and functionality. Furthermore, the hybrid materials are expected to have synergic effects which are not shown in just one component.

In this report, we fabricated new types of organic-inorganic hybrid thin films by molecular layer deposition. The hybrid thin films were made by sequential surface reactions of metal alkyls and bifunctional monomers. Diethylzinc and 2,4-hexadiyne-1,6-diol are used as an inorganic precursor and an organic precursor, respectively, in order to fabricate poly(zinc diacetylene). Some methods are used to characterize the microstructure and composition of the hybrid films such as Raman, XPS and TEM analysis. And, the electric and optical properties were analyzed by a TFT fabrication and photoluminescence spectroscopy, respectively. The high performance of TFTs, on/off ratio of over 10^7 and saturation electron mobility of over 10 cm2/V·s. The molecular layer deposition process can proceed under the low-temperature condition that indicates the possible use of hybrid films to flexible devices.

EM-MoP-4 High Performance Encapsulation Polymer-Al_2O_3 Hybrid Thin Layer by Atomic Layer Infiltration*, S Mo, **Hong Rho Yoon**, J Park, N Long, C Huong,* Hanyang University, Republic of Korea

Encapsulation is an important technology for isolating and protecting air-sensitive materials and is key in the development of new generation flexible electronic devices. Here we report an extremely high performance encapsulation hybrid thin layer prepared by filling the free volume of the polymer with Al2O3 using gas-phase atomic layer infiltration. The high density polymer−inorganic hybrid thin layer shows extremely low gas transmission rate, below the detection limit of the Ca corrosion test (water vapor transmission rate <10^(−7) g/m^(−2) day^(−1)). Furthermore, because of the remarkable nanometer-scale thinness of the complete polymer−inorganic hybrid, it is highly flexible, which makes it useful for encapsulation technology of new generation flexible devices.

EM-MoP-5 ALD of Metal Oxides Fabricated by using $La(NO_3)_3 \cdot 6H_2O$ Oxidant and their Applications*, **In-Sung Park**, S Kim, T Lee, S Seong, Y Jung, J Ahn,* Hanyang University, Republic of Korea

The oxide films with high-k including Al_2O_3, HfO_2, and ZrO_2 have been widely applied to dielectric of capacitor devices in fabrication of semiconductor memory. Recently, ALD method has been widely spreading to making the ultra-thin, dense, conformal, and widely-uniform deposition areas in spite of its very low productivity. In ALD process, the selection of oxidant is very important because of the variability of film characteristics such as growth rate, ALD temperature window, crystalline structure, contamination, and dielectric/electrical properties.

In this work, the using of $La(NO_3)_3 \cdot 6H_2O$ catalytic oxidant will be focused to fabricate HfO_2 films for insulator of resistor and dielectric of capacitor. The H_2O oxidant was used to make above films for the comparison. The devices with metal-insulator-metal structure were prepared and their electrical properties were also compared.

HfO_2 films were synthesized by ALD method using $Hf(NCH_3C_2H_5)_4$ precursor and $La(NO_3)_3 \cdot 6H_2O$ solution, which is catalyst and oxidant. The growth rate of HfO_2 film made with $La(NO_3)_3 \cdot 6H_2O$ solution is approximately three times faster than that with H_2O oxidant. The $La(NO_3)_3 \cdot 6H_2O$ solution effectively altered the surface roughness, crystalline status, and resistive switching properties of HfO_2 films. In spite of the same crystalline structure of both HfO_2 films made with $La(NO_3)_3\cdot 6H_2O$ and H_2O, the surface roughness of HfO_2 film grown by using $La(NO_3)_3\cdot 6H_2O$ solution oxidant is smoother than that using H_2O. Moreover, resistive switching characteristics of HfO_2 grown using $La(NO_3)_3\cdot 6H_2O$ was enhanced not only uniformity of switching parameters but also endurance.

EM-MoP-6 Bringing Higher Etch-resistance to Metal-infiltrated Polymer*,* ***Norikatsu Sasao****, K Asakawa, S Sugimura,* Toshiba Memory Corporation

Infiltration synthesis is an emerging technology that enables to realize organic-inorganic hybrid materials. The gaseous metal precursors penetrate into polymers followed by oxidation process, which stabilizes the metal derivatives into the polymer-matrix. Up to date, many fundamental studies have been carried out on the infiltration of trimethylaluminum(TMA) into polymethylmethacrylate(PMMA) thin films[1][2]. There has also been reported that TMA is selectively infiltrated to PMMA phase of the phase-separated block copolymer of PMMA and polystyrene, where etch-resistance of infiltrated PMMA is remarkably increased[3].

Although literatures show that TMA readily coordinates onto carbonyl group of the acrylate unit, the density of the resulting aluminum derivatives in PMMA is eliminated to the density of carbonyl groups. By increasing the carbonyl density in the monomeric unit of the polymer, we can expect to have higher aluminum content in the polymer after the infiltration process which could result in higher etch-resistance.

Recently we have synthesized a polymer having two or more carbonyl groups branched on the main-chain to increase carbonyl density compared to PMMA. Evidences show that TMA was infiltrated into the polymer at a higher density compared to that of PMMA and the etch-resistance increased as the aluminum content increased. Our novel strategy shows further pathways for future applications.

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[2]E. C. Dandley, C. D. Needham, P. S. Williams, A. H. Brozena, C J. Oldham and G. N. Parsons, "Temperature-dependent Reaction Between Trimethylaluminum and Poly(methyl methacrylate) during Sequential Vapor Infiltration: Experimental and *abinitio* Analysis," *J. Mater. Chem. C.*, 2014, 2, 9416

[3] R. Ruiz, L. Wan, J. Lille, K. C. Patel, E. Dobisz, D. E. Johnston, K. Kisslinger and C. T. Black, " Image Quality and Pattern Transfer in Directed Self Assembly with Block-selective Atomic Layer Deposition," *J. Vac. Sci. Technol. B*, 2012, 30(6), 06F202

EM-MoP-7 Magnetic and Electric Properties of Atomic Layer Deposited ZrO_2-based Thin Films*,* ***Kristjan Kalam****, H Seemen, P Ritslaid, T Jõgiaas, M Rähn, A Kasikov, A Tamm, K Kukli, M Mikkor,* University of Tartu, Estonia*; J Link, R Stern,* National Institute of Chemical Physics and Biophysics, Estonia*; S Dueñas, H Castán,* University of Valladolid

Multiferroic materials of simple stoichiometry may have prospective applications in memory and sensor technologies, especially if they could be produced at low temperatures over large-area substrates by ALD. Tetragonal or cubic sputtered ZrO_2 has found to be ferromagnetic [1], and, when combined with HfO_2 by ALD, behaved as a ferroelectric material [2]. Therefore, it is of interest to investigate if ZrO_2 coupled with another metal oxide would exhibit both ferroelectric and ferromagnetic hysteresis behavior in the same material sample.

We have studied, for instance, ZrO_2-Fe_2O_3 [3], ZrO_2-HfO_2 [4] and ZrO_2-Co_2O_3 [5] mixed layers or nanolaminates grown by ALD from $ZrCl_4$, $FeCp_2$, $HfCl_4$, $Co(acac)_3$, H_2O and/or O_3 mostly at 300 ^oC. The composition of the films could be controlled by varying the ratio of constituent metal oxide cycles. Structural evaluation revealed dominantly tetragonal or cubic ZrO_2. All oxides, as deposited, exhibited magnetization-field behavior characteristic of that in ferromagnetic materials. Most of the films in as-deposited states also showed certain remnant charge polarization in their charge-field dependences. The behavior could be strongly influenced by the charge transport and interfacial charge trapping. Certain ferroelectric component contributing to the polarization could not be neglected, although the charging was probably overwhelmed by leakage currents. Nonetheless, in some films, in particular ZrO_2-HfO_2, hysteresis loops implying both ferromagnetic and ferroelectric components in the materials could be observed. In this presentation, performance of different oxides as potential multiferroic host materials will be comparatively discussed.

[1] S. Ning and Z. Zhang, RSC Adv. 5 (2015) 3636.

[2] S. L. Weeks *et al*. ACS Appl. Mater. Interfaces, 9(15), 13440 (2017).

[3] K. Kalam *et al*., Beilstein J. Nanotech. 9 (2018) 119.

[4] K. Kalam, et al, ECS J. Solid State Sci. Technol. 7.9 (2018): N117-N122.

[5] K. Kalam, et al., Thin Solid Films 669 (2019) 294-300.

EM-MoP-8 Vapor Phase Infiltration as a New Approach in the Fabrication of Advanced Hybrid Thermoelectric Materials*,* ***Jaime DuMont****, M Knez,* CIC nanoGUNE, Spain

Hybrid organic-inorganic materials are rising stars in the field of thermoelectrics (TE), whose principal aim is to salvage the rejected heat of energy conversion processes by directly converting waste heat into electricity. With two-thirds of the 160 TWh required for global power consumption lost to the environment each year, the development of flexible, non-toxic, inexpensive and scalable TE materials would be of great economic and environmental interest. Realizing this ambition will require a new approach that can break away from the rare, toxic and expensive materials that have dominated the field until now.

This next generation of hybrid TE materials will require a synthesis strategy which 1) functions at temperatures low enough to not destructively act on the polymer 2) can tune the electrical and thermal conductivity of the hybrid material for optimal TE performance 3) maintain a strong chemical binding between the organic and inorganic components for long term stability and operational efficiency and 4) can be easily scaled for large-area applications. Vapor phase infiltration (VPI) is a technique primed to meet these requirements. In this work we will survey VPI processes of various transition metal compounds as a tool for the top-down fabrication of metal-poly(3-hexyl)thiophene (P3HT) hybrids as promising candidates for advanced TE materials. By monitoring the electrical conductivity and thermopower of these novel hybrid materials, we will show how the VPI process can be used to generate and optimize a new set of thermoelectric materials.

EM-MoP-9 Low-temperature Atomic Layer Deposition of Aluminum Oxide on Polymeric Powder Feedstocks for Improved Powder Rheology*,* ***John Miller****, C Gillespie, J Chesser,* Lawrence Livermore National Laboratory*; A Scheppe,* United States Air Force Academy*; A Nelson, N Teslich, A Lange, S Elhadj, R Reeves,* Lawrence Livermore National Laboratory

Some organic materials of interest in the additive manufacturing industry require inkjet/colloid based processes to avoid degrading the properties of the material of interest. Some of these organic feedstocks are cohesive in nature and tend to form agglomerates in suspensions, making them undesirable for use in additive manufacturing printing processes. Atomic Layer Deposition (ALD) can be used as a technique used to change the surface property of the material without changing the property of the bulk material of interest. ALD sequentially pumps reactive precursors into and out of a reactor vessel, which react on the surface of a desired substrate to form films with sub-nm level control. This paper studies the reduced temperature ALD deposition of aluminum oxide on polyimide/Si reference flats and melamine and nylon organic powder feedstocks for coating quality and its effect on the powder rheology and cohesivity. The result is a mixed amorphous phase aluminum oxide-hydroxide coating that is both highly uniform and conformal on the powder's surface. Alumina coatings on the nylon powders did not produce a significant change in the flow properties of the powder, due to the initial low cohesivity of nylon. The melamine however experienced significant improvements to flowability due to a reduction in cohesivity of the melamine feedstocks from the surface coating. Results show that thin coatings of 20 nm or less on these feedstocks can remarkably improve their surface chemistry for use in additive manufacturing processes.

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EM-MoP-10 Atomic Layer Deposition of Molybdenum Oxide Carbide and Molybdenum Carbide Films*,* ***Michael D. Overbeek****, C Winter,* Wayne State University

The atomic layer deposition (ALD) of Mo(O,C) and MoC films is described using $MoCl_5$ and the co-reactants oxalic acid or formic acid. Self-limited ALD growth was demonstrated at 350 °C for $MoCl_5$ and oxalic acid, however, the growth rate decreased at long $MoCl_5$ doses, consistent with etching. The growth rate of the $MoCl_5$ and oxalic acid process was 0.18 Å/cycle within an ALD window of 325-400 °C. The resistivities of the films decreased with increasing deposition temperature and was 366 μΩ cm for an 18 nm thick film grown at 400 °C. A plot of thickness versus number of cycles was linear with no nucleation delay. X-ray diffraction of the as-deposited films was consistent with nanocrystalline Mo(O,C). Atomic force microscopy of 18 nm thick films grown with $MoCl_5$ and oxalic acid in the

ALD window gave RMS roughnesses of 0.49-0.56 nm, indicating very smooth surfaces. X-ray photoelectron spectroscopy (XPS) showed Mo, O, and C in the films, with low levels of other elements. The films obtained using $MoCl_5$ and oxalic acid are thus Mo(O,C). Formic acid was also used with $MoCl_5$ as a co-reactant, since oxalic acid decomposes thermally at high temperatures to formic acid and CO_2. A plot of growth rate versus pulse length showed self-limited growth at 400 °C, but a plot of growth rate versus deposition temperature did not show an ALD window between 400-450 °C. Films grown with formic acid at 400 and 450 °C with thicknesses of 28.5 and 48.1 nm, respectively, showed RMS roughnesses between 0.55 and 0.88 nm. XPS of a film grown using $MoCl_5$ and formic acid at 450 °C showed a composition of MoC, with low oxygen and chlorine levels. The resistivity of a 48 nm thick MoC film grown at 450 °C with 1000 cycles was 177 µΩ cm.

EM-MoP-11 Solid Phase Epitaxy of ALD-Grown $PrAlO_3$ Films*, Navoda Jayakodiarachchi, W Waduge,* Wayne State University*; Y Chen, P Zuo, T Kuech, S Babcock, P Evans,* University of Wisconsin-Madison*; C Winter,* Wayne State University

An atomic layer deposition (ALD) process is reported for the growth of PrAlO3 thin films using tris(isopropylcyclopentadienyl)praseodymium (Pr(C5H4iPr)3), trimethylaluminum (AlMe3), and water. Pr(C5H4iPr)3 was chosen as a precursor because of its good volatility, high thermal stability, and high reactivity with water. Pr(C5H4iPr)3 was first evaluated as a precursor for the formation of Pr2O3 films using water as the co-reactant. Self-limited growth was demonstrated for pulse lengths of ≥3 s, with a growth rate of ~0.85 Å/cycle. An ALD window was observed between 275 and 350 °C, and the as-deposited Pr2O3 films were crystalline. The ALD growth PrAlO3 films was examined next on Si(100) and SiO2 substrates. Self-limited growth was demonstrated for Pr(C5H4iPr)3), AlMe3, and water at 300 °C using a 1:1 ratio of Pr(C5H4iPr)3) and AlMe3 pulses. An ALD window was observed from 275 to 325 °C with a growth rate of ~1.7 Å/cycle. The increase in film thickness as a function of the number of cycles at 300 °C was linear and showed a small nucleation delay. The as-deposited PrAlO3 films were amorphous, had smooth surfaces, and contained <0.5% carbon and chlorine, as analyzed by grazing incidence wide-angle X-ray scattering, X-ray reflectivity and atomic force microscopy, and X-ray photoelectron spectroscopy, respectively. The films grown with a 1:1 ratio of Pr(C5H4iPr)3) and AlMe3 pulses were slightly aluminum-rich (Pr:Al ~1.2-1.4) by electron probe microanalysis. As deposited PrAlO3 films grown on single crystal (100) SrTiO3 substrates at 300 °C were amorphous and annealing at 800 °C for 3 h resulted in fully crystallized PrAlO3 films. The crystallized PrAlO3 films were highly (001)-orientedwith a small population of polycrystalline grains with other orientations. The PrAlO3 00L and SrTiO3 00L reflections appeared on the same rod of reciprocal space, further indicating that the amorphous PrAlO3 film transforms into an epitaxial layer. The rocking curve width of the PrAlO3 (001) reflection was 9°. By contrast, PrAlO3 films deposited on Si(100) substrates with native SiO2 remained amorphous after annealing at 1000 °C for 8 h. The difference in the crystallization between PrAlO3 layers deposited on crystalline SrTiO3 and amorphous native SiO2 substrates indicates that PrAlO3 on SrTiO3 crystallized by solid phase epitaxy, in which the nucleation and orientation of the crystallized layer is set by the substrate.

EM-MoP-12 Homogenous Distribution of Dopants in ALD Films: Tin-Doped Zinc Oxide (ZTO) Case Study*, Triratna Muneshwar, D Barlage, K Cadien,* University of Alberta, Canada

ALD is a well-established thin film deposition technique where the material growth stems from the stacking of partial atomic monolayer in each surface reaction step. Being a bottom-up approach, doping of ALD could be readily achieved from introduction of dopant species during growth. For example, the most common approach for deposition of B-doped AO oxide growth, is to periodically deposit oxides AO with n_1 cycles and BO with n_2 cycles (super-cycle: $n_1 \cdot AO + n_2 \cdot BO$). Although the relative A/B content is precisely controlled with n_1 and n_2, the resulting multilayered structure would have a non-homogeneous dopant-B distribution (hence may require additional processing steps like annealing, ion bombardment, etc.). To overcome this limitation we demonstrate a method for homogeneously doped ALD films with BAOBAO… pulsing sequence. We show that the choice of dopant precursor, process parameter and also the sequence (ABO… or BOA…) are critical in controlling dopant concentration. As example we report our early results on tin-doped zinc oxide (ZTO) ALD films grown at 50 °C substrate temperature using tetraallyltin (TASn), diethyl zinc (DEZ), and a remote ICP O-plasma. We show that the pulsing sequence Sn/Zn/O gives a better control over Sn-content in ZTO films. With increasing Sn-content, measured room temperature electrical resistivity (ρ^{ele}) of as-grown ZTO films (each ~24 nm thick) was found to systematically decrease from 450 Ω-cm for ZnO, to 19.72 Ω-cm, 5.7×10^{-1} Ω-cm, and 2.8×10^{-2} Ω-cm for samples ZTO#1, ZTO#2 and ZTO#3 respectively.

EM-MoP-13 Uniform, Thermal ALD of Al_2O_3 and ZnO on Zirconia Particles*, Dhruv Shah, D Patel, J O'Tani, M Linford,* Brigham Young University

The technical literature contains relatively little on the topic of atomic layer deposition (ALD) on particles. Here we report thermal ALD of thin films of alumina and zinc oxide on zirconia powder substrates from trimethylaluminum and water, and diethylzinc and water, respectively. Very similar growth was obtained when ozone was substituted for water in these depositions. Depositions were optimized by varying the dose and purge times for the precursors with an aim to obtain uniform film thickness and growth per cycle (GPC). X-ray photoelectron spectroscopy (XPS) clearly showed an increase in surface aluminum and zinc with increasing numbers of ALD cycles. Transmission electron microscopy (TEM) showed uniform film growth and particle coverage. Film thicknesses were also measured on planar witness shards by spectroscopic ellipsometry (SE). Ultimately, up to 10 nm films of alumina and zinc oxide were grown on zirconia particles via 100 ALD cycles.

EM-MoP-14 Composition Control of Ge-Sb-Te Film by Supercycles of ALD GeSb and ALD Sb Followed by Tellurization Annealing*, Yewon Kim, J Lee,* Sejong University, Republic of Korea*; S Baik,* Hankyong National University, Republic of Korea*; W Koh,* UP Chemical Co., Ltd., Republic of Korea*; W Lee,* Sejong University, Republic of Korea

Phase change random-access memory (PCRAM) is getting attention as storage class memory (SCM) which is can fill the performance and cost gap between DRAM and NAND flash. Ge-Sb-Te (GST) compounds have been extensively studied due to their fast switching speed and high data retention. The GST thin films were prepared by physical vapor deposition, chemical vapor deposition and atomic layer deposition (ALD) techniques. As the mushroom structure changes to confined cell structure because of thermal interference, ALD technique is needed in order to deposit a thin film in a nano-size hole. Conventional ALD GST film was prepared with ALD GeTe and ALD Sb2Te3 supercycle. This method is complicated and deposited as amorphous during deposition, resulting in void formation during repeated PCRAM operation. In previous work, we prepared GST film by tellurization of ALD Ge-Sb. This process simplifies the supercycle ALD GST process and can form a crystalline GST thin film. Also, the incorporation of Te improves the gap fill characteristic by expanding the volume. Tellurization of the ALD Ge-Sb film could control the composition of Te by the tellurization temperature or the number of cycles, however it cannot control the composition ratio of Ge to Sb. Since the switching speed and durability of the phase change memory cell depend on the composition of the GST film, a method of controlling the composition ratio of Ge and Sb in the GST film is also required. In the present work, GST films with different compositions were prepared by ALD super-cycle process consisting of ALD Ge-Sb and ALD Sb. The composition ratio of Ge to Sb was controlled by changing the ratio of the sub-cycles. The temperature window and growth rate of ALD Ge-Sb and ALD Sb were investigated to determine the temperature and sub-cycle ratios of the super-cycle process. Ge-Sb films of different compositions were prepared by ALD super-cycle processes and then annealed in a tellurium atmosphere. The composition and phase transition temperature of the GST thin films were examined before and after the tellurium annealing. The phase transition temperature was tunable by controlling the subcycle ratio or tellurization conditions. Step coverage and gap filling characteristics were also investigated.

EM-MoP-15 Study on The Crystallinity and The Dielectric Constant of $Zr_xGe_{1-x}O_2$ Films using Mixed Zr - Ge Precursor by Atomic Layer Deposition *., Ju Young Jeong, Y Han, H Sohn,* Yonsei University, Korea*; H Noh, H Park,* SK Hynix Inc

Scaling of Dynamic Random Access Memory(DRAM) requires high k dielectric materials for data storage capacitor. ZrO_2 is favorite material for storage capacitors becasue of large band gap, low leakage current, good thermal stability. Dielectric constant of ZrO_2 depends on the crystal structure (monoclinic =19.7, cubic = 36.8, tetragonal=46.6). It was reported that doping of ZrO_2 with elements such as Mg, Ca, Y, La, and Ge enhances tetragonal phase of ZrO_2. In general, such elements are incorporated in ZrO_2 using laminated growth structure.

In this study, Ge-doped $ZrO\text{-}_2$ films were fabricated using mixed Zr-Ge precursor ($CpZr[N(CH_3)_2$

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. T itanicones 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.

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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.

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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.

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[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.

Emerging Materials
Room Grand Ballroom A-C - Session EM2-WeM

Organic-Inorganic Hybrid Materials

Moderators: Gregory N. Parsons, North Carolina State University, Jonas Sundqvist, Fraunhofer Institute for Ceramic Technologies and Systems IKTS

10:45am **EM2-WeM-12 Vapor Phase Infiltration: A Route for Making Insulating Polymer Fibers Conductive**, ***Mato Knez***, CIC nanoGUNE, Spain; *I Azpitarte,* CTECHnano, Spain

Future technological devices rely in large parts on flexible functional materials. Polymers play an important role for this approach as the combination of low weight and mechanical flexibility makes them unavoidable within this technological concept. However, for a variety of technological approaches, not only the mechanical properties, but also electronic properties of polymers need to satisfy the technological needs.

A promising strategy to implement conductivity into polymer fibers is based on vapor phase infiltration (VPI), if it was successfully applied for an infiltration of a conductive or semiconducting material. VPI is a modification of Atomic Layer Deposition (ALD) which allows synthesis of hybrid materials by infiltration of inorganic materials into organic substrate. With this technique diffusion of precursors into polymeric materials from the gas phase is enforced and yields new composites with inorganic moieties coordinated or covalently linked with the polymeric matrix.

Fibers of poly(p-benzamides), for example Kevlar®, are known since decades and are of great commercial importance primarily because of their exceptional mechanical strength and flexibility as well as an established industrial fabrication process. The polymer gains its mechanical properties through the high molecular order and the intermolecular hydrogen bonds, which in turn makes it very complex to introduce further functionalities into the material. This seriously limits the application range. For example, Kevlar is an electrical insulator and as such by default not suitable as active component in wearable electronic applications.

The present work shows a VPI-based approach towards functionalization of Kevlar fibers in two aspects. In the first instance, electrical conductivity of the intrinsically insulating fibers was induced. This was performed by infiltration of conductive metal oxides. In the second instance the resulting hybrid polymer-inorganic fibers became photocatalytically active upon irradiation with visible light. The photocatalytic effect relies on the insertion of ZnO into the fiber matrix and the chemical interaction between the inorganic and polymeric phase, which eventually result in back-doping of the ZnO with nitrogen hand in hand with the alteration of the electronic structure of the polymeric chain.

11:00am **EM2-WeM-13 Vapor Phase Infiltration of Metal Oxides into Microporous Polymers for Organic Solvent Separation Membranes**, ***Emily McGuinness***, *F Zhang, Y Ma, R Lively, M Losego,* Georgia Institute of Technology

Membrane-based organic solvent separations promise a low-energy alternative to traditional thermal separations but require advanced materials that operate reliably in chemically aggressive environments. While inorganic membranes can withstand demanding conditions, they are costly and difficult to scale. Polymeric membranes, such as polymers of intrinsic microporosity, are easily manufactured into form factors consistent with large-scale separations (e.g., hollow fibers), but perform poorly in aggressive solvents. Here, a new post-fabrication membrane modification technique, vapor phase infiltration (VPI) is reported that infuses polymer of intrinsic microporosity 1 (PIM-1) with inorganic constituents to improve stability while generally maintaining the polymer's macroscale form factor and microporous internal structure **(Figure 1)**. The atomic-scale metal oxide networks within these hybrid membranes protect PIM-1 from swelling or dissolving in organic solvents including: tetrahydrofuran, dichloromethane, and chloroform **(Figure 2a)**. This atomic-scale metal oxide network further decreases the molecular weight cutoff (MWCO; the smallest molecular weight the membrane "successfully" rejects) in n-heptane and toluene from a MWCO of about 600 g/mol for pristine PIM-1 thin film composite membranes to 204 g/mol for hybrid AlOx/PIM-1 membranes **(Figure 2b)**. The hybrid membranes further retain this MWCO and high levels of rejection (>95%) in solvents that traditionally swell or even dissolve pristine PIM-1 (such as ethanol and tetrahydrofuran). The decrease in MWCO and increase in stability of AlOx/PIM-1 hybrid membranes allows them to perform separations not only between solutes and solvents, but also separations of more challenging systems such as those comprising multiple solvents. For example, the hybrid AlOx/PIM-1 membranes are capable of enriching the toluene concentration in a mixture of 90 wt% toluene, 5 wt% 1,3,5-triisopropylbenzene, and 5 wt% 1,3-diisopropylbenzene from 90.0 wt% to 97.8 ± 0.3 wt%. In this talk, we will discuss the chemical mechanisms of the infiltration process that we believe create the hybrid structures necessary to support this enhanced stability and separation performance.

11:15am **EM2-WeM-14 ZnO-Infiltrated Hybrid Polymer Thin Films with Enhanced Gravimetric Water and Oxygen Vapor Sensing Properties**, *E Muckley, L Collins, A Ievlev,* Oak Ridge National Laboratory; *X Ye, K Kisslinger,* Brookhaven National Laboratory; *B Sumpter, N Lavrik,* Oak Ridge National Laboratory; ***Chang-Yong Nam***, Brookhaven National Laboratory; *I Ivanov,* Oak Ridge National Laboratory

Organic-inorganic hybrids generated by infiltration synthesis, a hybridization technique derived from atomic layer deposition (ALD), can feature various unique materials properties and functionalities not observed in conventional materials. In this work, we discover that the ZnO-infiltrated polymer hybrid nanocomposite thin film exhibits remarkably enhanced light-activated gravimetric gas vapor sensing properties. The hybrid nanocomposite thin film prepared by infiltrating molecular ZnO in SU-8, a common negative-tone, epoxy-based polymer resist, features up to 20-fold greater gravimetric responses to oxygen and water vapors compared with control ZnO or SU-8 thin films in a dark environment. Additional 50 – 500% enhanced responses are detected under ultraviolet (UV) irradiation. Experimental interrogation shows that the increased gravimetric response of the hybrid film is attributed not only to the higher analyte accessibility to active ZnO sites in the matrix but also to the reversible, light-induced increase of surface potential and adsorption energy. Density function theory calculations suggest that the UV enhancement is caused by the light-induced, reversible generation of hydrophilic fluoroantimonic acid from the photoacid generator (PAG) residual in the SU-8 film matrix. A gravimetric sensor based on the ZnO-infiltrated SU-8 hybrid finally enables 96% accurate classification of water and oxygen environments with sub-10 mTorr detection limits. The results highlight the utility of infiltration synthesis for advancing sensor technologies.

11:30am **EM2-WeM-15 Physically Interpenetrated Organic-Inorganic Sub-Surface Layers Created via Vapor Phase Infiltration for Improved Film Adhesion**, ***Mark Losego***, *S Dwarakanath, R Tummala,* Georgia Institute of Technology

Like atomic layer deposition (ALD), vapor phase infiltration (VPI) uses sequential pulsing of gaseous precursors to chemically modify a substrate. In VPI, these precursors sorb into the subsurface (bulk) of the polymer substrate, eventually becoming entrapped and forming a new organic-inorganic hybrid material. We have been studying the effects of just a few

(< 5) VPI exposure cycles on the structure and properties of various polymeric materials and often find that significant inorganic loading can be achieved through a single exposure step (from 2 wt% to up to 20 wt%). Beyond loading, the chemical structure of these materials is still not well understood. While in some cases, chemical bonding between the organic and inorganic components is evident, often we do not observe any chemical changes. For these materials, we believe the metal-organic precursor is forming an adduct to one of the polymer's functional groups, but upon exposure to a co-reactant (e.g., H_2O or O_2), the metal oxide cluster product becomes detached from the polymer. The resulting physically intertwined network of organic and inorganic constituents offers a unique hybrid structure with new property space to explore. This talk will focus on one such system, a redistribution layer (RDL) polymer used for electronic packaging infiltrated with AlO_x. We have found VPI of this RDL polymer can improve adhesion strength to metallic electrode layers by 3x (~200 g/cm for untreated versus ~600 g/cm treated). At failure, these infiltrated interfaces show bulk polymer fracture, indicating the polymer fails before the interface. Extensive spectroscopic investigations show no indication of change to the RDL polymer chemistry, suggesting that the inorganic is physically interpenetrated with the polymer chains creating a "root system" that improves adhesion through physical entanglement. Optimization of the VPI process temperature for adhesion will be discussed. Low process temperatures impede sufficient diffusion depth of the inorganic, while high process temperature preclude sufficient inorganic loading because sorption is thermodynamically limited.

11:45am **EM2-WeM-16 Inorganic-Organic Thin Film Layer-Structures and Thermal Conductivity**, ***Fabian Krahl,*** Aalto University, Finland*; A Giri, P Hopkins,* University of Virginia*; M Karppinen,* Aalto University, Finland

We utilize a combined atomic/molecular layer deposition approach to engineer layered ZnO-benzene structures that are meant to show precisely tailorable thermal conductivity values. We deposit a wide range of different layer sequences from regular superlattices to linear gradients (a linear increase in the space between benzene layers) and even more complex layering structures (see attached picture).

In superlattice structures with 12 benzene layers the thermal conductivity is effectively suppressed by decreasing the thermal conductivity from around 54 W $m^{-1}K^{-1}$ in pure ZnO down to values of around 4 W m^{-1} K^{-1}[1,2]. The thermal conductivity in the ZnO-benzene system is most probably suppressed by scattering the phonons that are responsible for the heat conduction in ZnO [2,3]. We are investigating deviations from the superlattice structure and reported our first findings last year [4], more samples are currently measured. We want to understand the connection between the films thermal conductivity and their internal structure to design materials with a high electrical but low thermal conductivity which would be of tremendous use for thermoelectric devices.

References

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Emerging Materials
Room Grand Ballroom E-G - Session EM3-WeM

Epitaxial Growth and III-V Materials

Moderator: John Ekerdt, University of Texas at Austin

10:45am **EM3-WeM-12 Atomic Layer Epitaxy of Zinc Oxide on C-plane Sapphire from Diethylzinc and Water using Pulsed-Heating Atomic Layer Deposition**, ***Brandon Piercy,*** *M Losego,* Georgia Institute of Technology

A challenge to atomic layer epitaxy (ALEp) is the mismatch between low-temperature windows for certain ALD precursors and the higher thermal budgets required for epitaxial growth. A common solution is to use precursors with higher ALD temperature windows, but these do not necessary exist for all desired chemistries. Therefore, ALEp is limited to material combinations having low lattice mismatch and high temperature precursor stability. To circumvent this challenge, we are exploring a new technique called pulsed-heating ALD (PH-ALD) that interleaves individual ALD growth cycles with a fast, high-temperature heat pulse using a high-power resistive heater. As proof-of-concept, we study epitaxial growth of ZnO on c-plane sapphire using a diethylzinc (DEZ) / water chemistry. DEZ is known to decompose above about 180˚C, and the DEZ-H_2O system cannot be grown epitaxially on c-sapphire with traditional thermal ALD approaches. Here, we explore the use of pulse heating to temperatures of up to 900˚C and for various ALD cycle ratios. X-ray diffraction shows the best epitaxial alignment and ZnO rocking curve, with a FWHM of <0.5˚, at a pulse temperature of 900˚C and a 1:1 ALD:heat pulse ratio. Crystal quality and intensity drop significantly with pulse temperatures less than 800˚C. Reducing the ALD cycles:heat pulse ratio also lowers crystal quality, but epitaxial growth is retained down to 5 ALD cycles per heat pulse. Photoluminescence spectroscopy of the D0x band shows that the 1:1 PH-ALD samples have 1.3x the intensity of post-annealed ZnO ALD and 10x the intensity of as-deposited ZnO ALD. Finally, we study growing a few layers of PH-ALD ZnO followed by standard thermal ALD with no pulsed heating. We find that a template layer of only 20 PH-ALD cycles is sufficient to template ZnO epitaxial films up to 100 nm thick.

11:00am **EM3-WeM-13 Growth of AlN Barriers in Al/AlN/Al SIS Josephson Junctions by Low Temperature Atomic Layer Epitaxy**, ***Charles Eddy, Jr.,*** U.S. Naval Research Laboratory*; D Pennachio, J Lee, A McFadden,* University of California, Santa Barbara*; S Rosenberg,* U.S. Naval Research Laboratory*; Y Chang, C Palmstrom,* University of California, Santa Barbara

Superconductor-Insulator-Superconductor (SIS) structures are of increasing interest for the creation of Josephson junctions that can serve as the basis for quantum qubit transmons, which hold significant promise for quantum computing technologies. Traditionally, these devices have been developed using amorphous AlO_x in Al/AlO_x/Al structures and have enabled fundamental demonstrations of transmon performance. However, improved performance may be expected with an epitaxial insulator. Even in these structures, the nature of the superconductor/substrate interface and the superconductor/ambient interface limits coherence and, consequently, qubit performance.

In an effort to address this challenge, we employ low temperature atomic layer epitaxy (ALEp) to grow crystalline AlN insulators on crystalline aluminum films. Smooth epitaxial aluminum films are grown by evaporation on cryogenically-cooled, buffered GaAs(001) substrates [1]. These epitaxial surfaces are "frozen" using a low temperature nitridation atomic layer process (ALP) before the samples are ramped to 300° C for low temperature ALE of AlN using semiconductor grade trimethylaluminum and UHP argon and nitrogen inductively coupled plasmas (ICPs). In this study, we evaluate the structural effects of variations in the initial nitridation ALP, growth conditions of ALEp AlN barriers, and SIS barrier thickness using transmission electron microscopy. We have found that at one end of the spectrum, a simple 5 cycle nitridation ALP of epitaxial aluminum at ~90° C, where each cycle is a 30 second exposure to 300W UHP argon/nitrogen (200/75 sccm) ICP , consumes a significant fraction of the aluminum to make an amorphous AlN insulator that is roughly 2 nm thick. When this surface is subjected to another low temperature Al evaporation, the top Al films are a mixture of amorphous and polycrystalline. When the same nitridation ALP is employed and followed by 5nm of ALEp AlN growth at 300° C, a similar amount of the aluminum film is consumed and an amorphous ALEp AlN layer results. Finally, when the nitridation ALP is reduced to a single cycle of nitridation, less of the aluminum film is consumed and the 5nm AlN ALEp film shows polycrystallinity with small regions demonstrating sharp, potentially epitaxial interfaces. This result suggests that proper ALP nitridation of the epitaxial aluminum can support epitaxial growth of AlN by ALE. Further studies of the influence of number of cycles, cycle duration, plasma chemistry and plasma power on both the nitridation ALP and AlN ALEp will be presented.

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11:15am **EM3-WeM-14 Investigating Plasma Parameters and Influence of Argon to the Crystallinity of GaN Films Grown by Plasma-Assisted ALD**, ***Deepa Shukla,*** *I Saidjafarzoda, A Mohammad, B Brian Willis, N Biyikli,* University of Connecticut

Gallium nitride has attracted significant attention in (opto)electronic and RF-chip industry mainly due to its wide bandgap of about 3.4 eV,which revolutionized lighting as well as high-power and high-frequency electronic devices. However, conventional crystal growth methods employ substrate temperatures typically around ~1000 °C, which is incompatible with post-CMOS integration and other temperature-sensitive substrates. To broaden the application spectrum of GaN, lower temperature growth methods are highly needed. Plasma-assisted ALD (PA-ALD) is a strong candidate which also provides unmatched conformality and uniformity performance. In this work, GaN thin films were grown on Si (100) substrates using PA-ALD. Trimethylgallium (TMG) and N2 /H2/Ar plasma were used as metal precursor and co-reactants. GaN deposition experiments were performed with and without Ar plasma at different plasma powers (150W, 175W, 200W) and different temperatures ranging within 120-240°C. An optimal growth per cycle (GPC) of ~0.7Å was observed at 150°C using in-situ ellipsometer and was confirmed by ex-situ x-ray reflectivity (XRR) analysis. The hexagonal wurtzite crystal peaks were observed in the grazing-incidence x-ray diffraction (GI-XRD) analysis. Among the films deposited, GaN samples grown at 240°C showed crystalline character with a preferred orientation along the (002) plane signifying GaN crystal formation temperature above 200°C. Moreover, the absence of Ar gar in the plasma showed a notable reduction in the peak intensities of (100) and (101) crystal domains, resulting in a predominantly preferred (002) orientation. Effect of plasma power and plasma duration on the quality of GaN was carried out with N2/H2-plasma during deposition cycles. No considerable change in crystal orientation was observed with change in plasma power, however increase in plasma duration from 10 to 40 sec suppressed the formation of (100) and (101) domains, resulting in a dominant (002) diffraction peak.

11:30am **EM3-WeM-15 Ultrathin GaN Epilayer by Low-temperature Atomic Layer Annealing and Epitaxy***, **Wei-Chung Kao**, W Lee, Y Yin,* National Taiwan University, Republic of China*; J Shyue,* Academia Sinica*; H Lin, M Chen,* National Taiwan University, Republic of China

Conventionally, GaN epilayers have been grown by metal-organic chemical vapor deposition (MOCVD) at very high growth temperatures (>1000°C) in order to achieve high crystal quality. However, the high-temperature growth technique is challenged by thermal stress and cracking due to the large difference in thermal expansion coefficients between GaN and the substrate. In this research, high-quality GaN heteroepitaxy has been achieved by atomic layer annealing and epitaxy (ALAE) at a low growth temperature of 300°C. By introducing a layer-by-layer, *in-situ* He/Ar plasma treatment at a low plasma power in each cycle of atomic layer deposition, the crystal quality of the GaN is significantly enhanced. The significant improvement of the GaN crystal quality is attributed to the effective annealing effect due to ion bombardment from the He/Ar plasma to each as-deposited layer. The nano-beam electron diffraction, high-resolution transmission electron microscopy, and atomic force microscopy reveal a high-quality nanoscale single-crystal GaN epilayer with a very smooth surface. The full width at half-maximum of the X-ray rocking curve of the GaN epilayer is as low as 168 arcsec. This research demonstrates the impact of the low-temperature ALAE technique for growing high-quality nanoscale GaN epilayers for high-performance solid-state lighting, solar cells, and high-power electronics.

11:45am **EM3-WeM-16 High Quality ALD Formation of Group-III Nitrides and their Applications in FTO-based Thin Film Solar Cells***, **Xinhe Zheng**, H Wei, P Qiu, M Peng, S Liu, Y He, Y Song, Y An,* University of Science and Technology Beijing, China

Group-III nitrides semiconductors (GaN, AlN, InN), grown by high-temperature MOCVD or MBE methods, have been widely utilized in optoelectronic and microelectronic devices. However, due to some benefits like low deposition temperature, precise thickness control and good conformality, ALD has recently attracted much attention in the fabrication of group-III nitrides materials. Here, we report high-quality growth of nitrides using plasma-enhanced ALD (PEALD). By optimizing the ALD window parameters, a single-crystalline nitride thin film can be achieved. Their optical, electrical, structural properties and impurities content are in detail characterized.

For some thin film solar cells using FTO glass substrates, interface modification and/or carrier transportation have been mainly focused for the improvement of device performance. So far, various metal oxides (TiO_2, Al_2O_3, ZrO_2, SiO_2, etc) deposited by ALD have been used in the CIGS and perovskite solar cells. However, there are still no reports about the application of group-III nitrides in FTO-based thin film solar cells using quantum dots (QDs) and perovskite compounds as solar energy materials. In this study, we successfully fabricate high quality GaN and AlN onto the FTO glass substrates at a very low temperature by PEALD. It was found that the existence of ultrathin AlN coating can efficiently reduce quantum loss in the interface between TiO_2 and CdSeTe QDs. An enhancement of open-circuit from 0.642 V to 0.679 V, corresponding to an increase of conversion efficiency from 8.51 % to 9.31% under AM 1.5G irradiance, is achieved for an insertion of AlN. The results show that the ultra-thin AlN layer on TiO_2/QDs surfaces can create an energy barrier for electron injection from QDs into the electrolyte and the injected electron from TiO_2 into the electrolyte, thus effectively inhibiting photo-generated electron recombination. The ALD GaN thin film on FTO glass here could serve electron transport layer for perovskite solar cells. The results indicate that GaN thin-film thickness has a significate effect on the electron transport and collection of the photovoltaic cells. It is found that the devices based on the 50-cycle GaN thin-film (~4 nm) show the best cell performance with efficiency of 15.2%. The introduction of group-III nitrides has shown promise for improving solar cell performance and could open up a way in designing novel thin film solar cells.

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Emerging Materials
Room Regency Ballroom A-C - Session EM1-WeA
Ternary and Quaternary Oxide Materials

Moderator: Bart Macco, Eindhoven University of Technology

1:30pm **EM1-WeA-1 Rhenium(III)-based Ternary Oxides: Novel Materials from Straightforward Synthesis *via* ALD Comprising Uncommon Reaction Pathways***, **Max Gebhard**, S Letourneau, D Mandia, D Choudhury, A Yanguas-Gil, A Mane, A Sattelberger, J Elam,* Argonne National Laboratory

Oxides of rhenium, such as ReO_2 and ReO_3, exhibit high conductivity in the order $\sigma = 10^3 - 10^4$ $(\Omega cm)^{-1}$, close to that of metals. This property is of high importance regarding applications with high demands on tailored electrical properties. An example of such an application are microchannel plates (MCPs), which are used as signal amplifiers in advanced detector units for UV-light (space aviation) and photoelectrons (XPS). Also, MCPs play a crucial role in the development of large area photodetectors.[1] MCPs are comprised of a glass capillary array. By applying a material with high secondary electron emission (SEE) yield, an incident electron/photon can create an electron avalanche that eventually increases the signal-to-noise ratio and thereby allows the detection of event starters. Below the SEE layer, a resistive coating must be applied, exhibiting the right range of resistivity to avoid electrons from being drained and to act as electron supplier. This material must be operable at elevated temperatures, *i.e.* it must have a low temperature-coefficient of resistance (TCR) to avoid decreased device performance at higher temperatures. Metal nanoparticles embedded in an Al_2O_3-matrix have been shown to provide the right resistivity for MCP application.[2] However, their TCR values demand for the development of materials with improved properties.

In this context, the development of ternary oxides, comprising ReO_x units with electrical conductivity and other components with dielectric character, provide a good opportunity to overcome the limitations of existing coatings.

Herein, we present two new materials, namely $ReAl_yO_x$ and $ReSi_yO_x$. These materials, where $ReSi_yO_x$ is reported for the first time, have been deposited using ALD and detailed mechanistic studies revealed that during the growth, reductive elimination reactions cause the formation of uncommon but stable Re(III) oxide species. Furthermore, fascinating mechanisms allowing the formation of unsaturated hydrocarbons and hydrogen, were identified during the growth. The processes were explored in great detail employing *in-situ* tools such as QCM, QMS and FTIR. Furthermore, the materials were fully characterized in terms of composition, structure, and electrical properties using XPS, RBS/HFS, XRD, XRR and XAS.

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[2] J. W. Elam, A. U. Mane, J. A. Libera, J. N. Hryn, O. H. W. Siegmund, J. McPhate, M. J. Wetstein, A. Elagin, M. J. Minot, *et al.*, *ECS Trans*. **2013**, 58 (10), 249

1:45pm **EM1-WeA-2 Growth Bbehavior and Electronic Characterization of $PbZrO_3$ and $PbZr_xTi_{1-x}O_3$ Grown by Atomic Layer Deposition with Several Zr Precursors***, **Nicholas Strnad**,* University of Maryland*; D Potrepka,* U.S. Army Research Laboratory*; A Leff,* General Technical Services, LLC*; J Pulskamp,* U.S. Army Research Laboratory*; R Phaneuf,* University of Maryland*; R Polcawich,* U.S. Army Research Laboratory

Process, structural, chemical, and electrical characterization is presented for $PbZr_xTi_{1-x}O_3$ (PZT) deposited by ALD using different combinations of precursors with thicknesses suitable for piezoelectric microelectromechanical systems (piezo-MEMS). PZT grown by ALD is desired for integration into 3-D MEMS [1] whereby actuators are grown on high aspect-ratio sidewalls, which greatly increases the areal work-density. To determine the viability of ALD PZT for MEMS, the films were integrated into micromachined, released cantilever structures. ALD $PbTiO_3$ (PTO) has been previously grown using lead bis(3-N,N-dimethyl-2-methyl-2-propanoxide) [Pb(DMAMP)$_2$] and tetrakis dimethylamino titanium [TDMAT] as the lead and titanium cation precursors, respectively [2]. Incorporation of tetrakis dimethylamino zirconium [TDMAZ] yielded PZT, but the growth rate of $PbZrO_3$ (PZO) and PZO-rich PZT was suppressed compared to PTO-rich PZT, resulting in a Zr/Ti composition less than the desired morphotropic phase boundary (MPB) composition of 52/48. The PTO-rich ALD PZT (Zr/Ti = 22/78) films were annealed at 700 °C in O_2 to crystallize into the perovskite phase. Micromachined trench structures 45 µm deep were coated with conformal ALD $PbZr_{22}Ti_{78}O_3$ to demonstrate that the process conditions fell within the ALD-window. Transmission electron microscopy images revealed that the ALD PZT films crystallized with grains tens of nanometers in diameter. Rutherford backscattering was used to characterize the chemical composition of the films. In-situ ellipsometry indicated that the as-grown PZT thickness was a linear function of the number of supercycles. For 200 nm-thick ALD $PbZr_{22}Ti_{78}O_3$ films, planar metal-insulator-metal capacitors were created to evaluate the ferroelectric and dielectric properties. The films exhibited an average remnant polarization of 20 µm/cm^2, a dielectric constant at zero volts of 475, a tuning range of 212-548 from 0 to 450 kV/cm, and a corresponding Tan delta of 0.025 (see supplemental). The ferroelectric properties of the ALD PZT presented here rivals PZT grown at similar compositions and thicknesses by other well-accepted processing methods. Several other zirconium precursors were investigated for inclusion into ALD PZT including zirconium tert-butoxide [Zr(OtBu)$_4$] and tetrakis ethylmethylamino zirconium [TEMAZ]. The incorporation of Zr(OtBu)$_4$ led to improved tunability of the zirconium concentration but also resulted in a lower overall growth rate of PZT.

References

[1] Three dimensional piezoelectric MEMS, US8966993 B2, J.S. Pulskamp and R. G. Polcawich (19 Dec 2012)

[2] N. A. Strnad et al. *J. Vac. Sci. Technol. A* 37(2) Mar/Apr 2019

2:00pm **EM1-WeA-3 Understanding Growth Characteristics of ALD $NiAl_yO_x$: The Role of Ozone***, **Jonathan Baker**, J Schneider, S Bent,* Stanford University

ALD of ternary films has grown in interest as applications requiring the advantages of ALD (including sub-nanometer thickness control, uniformity, compositional control and conformality) have demanded more complex materials. However, depositing ternary materials by ALD is typically more complicated than the binary ALD systems from which the ternary materials are derived. As a result, the growth of a ternary material by ALD often deviates from ideal growth behavior described by the "rule of mixtures." In this work, ALD of $NiAl_yO_x$ was studied using the nickelocene ($NiCp_2$)/O_3 and trimethyl aluminum (TMA)/H_2O precursor systems for nickel oxide and aluminum oxide respectively. Depositions of $NiAl_yO_x$ were performed using the supercycle method, allowing a wide range of compositions to be achieved by altering the cycle ratio of nickel oxide to aluminum oxide ALD cycles. However, composition as a function of cycle ratio was found to be nickel deficient compared to the ideal rule of mixtures. The cause of the observed non-ideality was explored to help elucidate the ALD reaction mechanisms. Characterization of the films revealed that the growth rate of aluminum oxide was significantly enhanced following a $NiCp_2$/O_3 cycle. Modification of the rule of mixtures to account for the enhanced growth rate of Al_2O_3 resulted in a model which fits observed properties well, accounting for both the observed compositions and growth rates. In addition, $NiAl_yO_x$ has shown to be an interesting case study for understanding the deposition of ternary materials of first-row transition metal oxides grown with O_3. Similar to ALD of Fe_2O_3 and MnO_x, which utilize metallocene-derivatives and O_3, NiO ALD requires long precursor and O_3 exposures to achieve fully self-limiting growth. The root cause for this behavior is hypothesized to stem from the use of the strong oxidizer O_3, which may oxidize the metal centers to higher oxidation states or otherwise introduce extra oxygen into the film. For the deposition of $NiAl_yO_x$, low O_3 exposures were used to develop the initial $NiAl_yO_x$ system. To understand the effects of O_3 exposure on the deposition of the ternary ALD film and binary NiO system, growth of $NiAl_yO_x$ as a function of O_3 exposure was explored with an aim to understand the ALD reaction mechanisms at play when using O_3 as an oxidizer. The effect of high O_3 exposures will be discussed.

2:15pm **EM1-WeA-4 Atomic Layer Deposition of $B_xMg_{1-x}O$ Films: Progress Towards Shallow Boron Doping***, **David Mandia**, D Choudhury, M Gebhard,* Argonne National Laboratory*; J Liu,* Northwestern University*; A Yanguas-Gil, A Mane, A Nassiri, J Elam,* Argonne National Laboratory

Preparation of $B_xMg_{1-x}O$ films through an ABC-type ALD program employing bis(cyclopentadienyl) magnesium (II), trimethyl borate ($B(OCH_3)_3$), and water as precursors is presented herein. The thin film properties are extensively characterized by X-ray photoelectron (XPS), diffraction (XRD), and reflectivity (XRR). Moreover, optical properties of the as-grown and post-deposition annealed films are assessed through spectroscopic ellipsometry measurements with a particular focus on the effective optical properties of the B_2O_3 film component, which is an attractive shallow-boron dopant source material. Instead of using the highly toxic diborane (B_2H_6) as a boron doping source, the present work employs ALD to generate MgO-stablized $B\text{-}_2O_3$. Interestingly, as observed from *in-situ* quartz crystal microbalance (QCM) and Fourier transform infrared (FTIR) analysis, stabilization of B_2O_3 occurs by dosing $Mg(Cp)_2$ after the $B(OCH_3)_3$ pulse which forms Mg-B-O* surface species that undergoes further reaction to B_2O_3 in the succeeding water pulse. Without the $Mg(Cp)_2$ pulse (or MgO "AB" sub-cycle) preferential formation of boric acid ($B(OH)_3$) occurs instead of $B\text{-}_2O_3$. Post-deposition annealing treatments along with follow-up spectroscopic ellipsometry and high-resolution XPS/depth profiling measurements were performed to characterize the composite films' optical and electronic structural properties, respectively. The thermal ALD synthesis of $B_xMg_{1\text{-}x}O$ composite films on silicon in concert with post-deposition annealing is a potentially viable approach towards shallow-boron dopant layer or junction formation through the stable B_2O_3 component and could find use in solid-state electronics applications.

2:30pm **EM1-WeA-5 Enhanced Doping Control of Metal Oxide Thin Films Using a Modified ALD Process***, E Levrau,* IBM TJ Watson Research Center*;* ***Yohei Ogawa****,* ULVAC, Japan*; M Frank, M Hopstaken, E Cartier,* IBM T.J. Watson Research Center*; K Schmidt,* IBM Research - Almaden*; M Hatanaka,* ULVAC, Japan*; J Rozen,* IBM T.J. Watson Research Center

The introduction of controlled amounts of dopants into logic and memory devices has been extensively used in nanoelectronics in order to alter the properties of a material and make it suitable for a specific application. Doping thin films can be complicated because of the difficulty to control thickness and dopant gradient distribution.

Atomic Layer Deposition allows for excellent thickness control and doping is usually achieved by varying the cycle ratio of two metal oxides during deposition, M1O and M2O, in what are called super-cycles. We refer to this method as the standard nanolaminate process [1]. Here, we propose a modified ALD process that allows for finetuning the dopant concentration down to a few atomic % in the metal oxide (MO) thin film. This doping control can happen at thicknesses much thinner than standard nanolaminates thus allowing for a better trade-off between stack functionality and leakage. Doping levels of less than 10cation% are desired, specifically for higher k phases of HfO_2 for ferroelectric devices [2].

In figure 1, a comparison of the minimum deposition thickness required for each method, is given for varying dopant concentrations. This illustrates that the modified ALD process allows for films to be ~6x thinner than the standard nanolaminate process from the studied precursors for Zr-doped HfO_2, while exhibiting less than 5% 1-sigma thickness variation across a 200mm wafer. The process does not involve BEOL thermal budget or partial reactions associated with plasma oxidation and can therefore be very conformal. This makes it compatible with FEOL integration for 3D thin film depositions.

It has been demonstrated that doping can be beneficial for non-volatile memories as it can enhance the endurance and the switching stability of the devices [3]. Here, HfZrO thin films with varying dopant levels of Zr are deposited through the modified ALD method on 200mm substrates. Dopant concentrations are determined by RBS analysis. Film properties are analyzed with spectroscopic ellipsometry and XPS. Thin-film HfO_2-based ferroelectric devices with different dopants will be evaluated.

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2:45pm **EM1-WeA-6 As Deposited Epitaxial $LaNiO_3$ and $La(Ni,Cu)O_3$ with Controllable Electric Properties***,* ***Henrik Hovde Sønsteby****,* University of Oslo / Argonne Natl. Labs, Norway*; O Nilsen, H Fjellvåg,* University of Oslo, Norway

Depositing complex oxides by ALD is a rapidly emerging field, with new materials with excellent properties published every month. $LaNiO_3$ is a perovskite type oxide with metallic behaviour, thought to play a major role in functional multilayer stacks and integrated electronics. Although routes for depositing $LaNiO_3$ has been reported in literature, an annealing step has always been necessary to obtain eptaxial films. In many applications this hinders monolithic device integration, and can cause unwanted strain effects and cracking.

In this presentation we show a facile route for direct epitaxial growth of $LaNiO_3$ by thermal ALD at temperatures as low as 250 °C. The films show excellent conductive properties as deposited, with specific resistivity as low as 10^{-4} Ohm cm. The functional properties of the films are slightly improved upon annealing, reaching specific resitivites in the 10^{-5} Ohm cm order of magnitude. Furthermore, we show that the order of precursor pulses plays a fundamental role in obtaining high quality as deposited epitaxial films.

$LaNiO_3$ is a remarkable member of the $RENiO_3$ series of materials (RE = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Y, Lu),as it is the only member that remains metallic to 0 K. All other members observe a metal-insulator-transition (MIT) at temperature varying from ~100 K (Pr) to ~600 K (Lu). Controllably tuning the MIT is highly awaited by the community.

In this presentation we also show how substution by Cu on the Ni-site alters the electric properties and MIT temperature of $LaNiO_3$. We show that a full range of compositions is attainable, from $LaCuO_x$ to $LaNiO_3$, and that the electronic properties vary smoothly over this composition range. ALD can be used to obtain a remarkable cation composition control. Furthermore, we hypothesize on the reason behind the varying properties of this material system, and try to explain it by showing how oxygen vacancies are introduced by copper substitution. This may help shed light on the surprising properties of $LaNiO_3$ itself, but more importantly the films can be directly used in applications where a tunable MIT is necessary.

This presentations highlights the use of complex oxide ALD as a real alternative to MBE, with several key advantages such as conformality and low temperature deposition.

3:00pm **EM1-WeA-7 Time Dependence of Pyroelectric Response in Ferroelectric $Hf_{0.58}Zr_{0.42}O_2$ Films***,* ***Sean Smith****, M Henry, M Rodriguez,* Sandia National Laboratories*; J Ihlefeld,* University of Virginia

HfO_2 based ferroelectrics are a promising family of ferroelectrics stable as thin films. The ferroelectric response in HfO_2 thin films is associated with a metastable orthorhombic phase, typically seen in films < 30 nm thick, stabilized by doping, electrode material, deposition conditions and annealing. Thin HfO_2 based ferroelectrics are attractive for use in memory, energy harvesting, and sensing applications, however the polarization response of the thinnest of these films, <~5 nm, has been reported to be unstable over time. In this work we show that the pyroelectric response of 5 nm $Hf_{0.58}Zr_{0.42}O_2$ with TaN electrodes decreases logarithmically after biasing, decreasing from an initial value of -58 $\mu Cm^{-2}K^{-1}$ to ~-40 $\mu Cm^{-2}K^{-1}$ in the first 24 hours. While films 10 nm and thicker have a pyroelectric response that is constant on the same timescale.

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3:15pm **EM1-WeA-8 Tailoring Nickel Oxide Conductivity by Introducing Transition Metals: From First-principles to Experimental Demonstration***,* ***Md. Anower Hossain****, T Zhang, D Lambert,* University of New South Wales, Australia*; Y Zakaria,* Hamad Bin Khalifa University, Qatar*; P Burr,* University of New South Wales, Australia*; S Rashkeev, A Abdallah,* Hamad Bin Khalifa University, Qatar*; B Hoex,* University of New South Wales, Australia

Transition metal oxides, such as MoO_3, WO_3, V_2O_5, and NiO have shown potential for application as hole-selective passivating contact for silicon (Si) solar cells. Among them, NiO is a p-type semiconductor which possesses notoriously poor hole-conducting properties. Doping of metal oxides with multivalent metal cations is one of the most effective ways to improve electronic band structure properties of resulting ternary metal oxides because dopants create favorable defect states crucial for charge carrier transport. Therefore, we used first-principles density functional theory (DFT) computations as a predictive tool to identify suitable dopants. The density of states, defect formation energies, and thermodynamic transition levels of various charge states within the band gap of doped NiO were calculated and promising dopants were identified. We synthesized Al-doped NiO ($Al_xNi_{1\text{-}x}O$) and Zn-doped NiO ($Zn_xNi_{1\text{-}x}O$) films onto 2.0 Ω.cm *p-Si* wafers using atomic layer deposition (ALD). We used a supercycle approach alternating *N* (10, 25, 50) NiO cycles and 1 Al_2O_3 cycle. Cross-sectional transmission electron microscopy and energy dispersive x-ray spectroscopy mapping showed conformal films with the elemental distribution of Ni, O, and Al. X-ray photoelectron spectroscopy (XPS) measurements revealed the presence of Ni^{2+}, Ni^{3+} and Al^{3+} oxidation state in the films. The Al content was found to scale with the number of AlO_x ALD cycles. The density of the Ni^{3+} and Al^{3+} oxidation state increased with the increasing number of AlO_x ALD cycles, confirming the Al incorporation into the host lattice of NiO. However, a significantly higher Al concentration was found in the $Al_xNi_{1\text{-}x}O$ film as was expected from the supercycle ratio. This was resulting from a significantly higher growth per cycle of AlO_x compared to NiO. While undoped NiO was found to be resistive, the $Al_xNi_{1\text{-}x}$ films showed the contact resistivity of 41.6 - 113 $m\Omega{\cdot}cm^2$ after annealing in a rapid thermal processing furnace at 200-300 °C under N_2 for 10 minutes. In addition, the $Zn_xNi_{1-x}O$ films deposited by supercycle of NiO and ZnO cycle also showed the Ohmic contact with *p-Si*. The $Zn_xNi_{1-x}O$ films were also thermally stable up to 500 °C with the best contact resistivity of approximately 21.5 $m\Omega\cdot cm^2$. This indicates a significant improvement of contact performance as compared to the undoped NiO counterparts. This work demonstrates that a ternary $Al_xNi_{1-x}O$ and $Zn_xNi_{1-x}O$ films are suitable hole-selective passivation contact for the *p-Si* solar cells.

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