Emerging Materials
Room 113-115 - Session EM-MoA

Laminate, Multicomponent, and Nitride Materials

Moderators: Nicholas Strandwitz, Lehigh University, Ji Hye Kim, ISAC Research Inc.

4:00pm **EM-MoA-11 Comparisons Between TiO_2/Al_2O_3 Nanolaminates Grown by Thermal and Plasma Enhanced Atomic Layer Deposition: Growth Mechanism and Material Properties***, G Testoni,* Universidade do Vale do Paraíba, Brasil*; **Rodrigo Pessoa**, M Fraga,* Universidade Brasil, Brasil*; N Galvão,* Instituto Tecnológico de Aeronáutica*; W Miyakawa,* Instituto de Estudos Avançados*; H Maciel,* Instituto Tecnológico de Aeronáutica

Nanolaminate coatings can offer significant improvements to traditional single-layer materials. An interesting class of nanolaminate materials is one based on alternatively ordered thin films of transition metal oxides with nanoscale thickness [1]. Using the TiO_2/Al_2O_3 nanolaminate concept of our previous work [1], it is possible to obtain at high temperature a 'stable amorphous film' which is very attractive for applications in microelectronics and optics. It is known that amorphous films of certain materials 'crystallize' during the various processing steps (deposition, metallization and lift-off) required for manufacturing a device. This crystallization modifies the fundamental properties of the film, which makes it suitable for the application. Herein, the thermal atomic layer deposition (ALD) and plasma enhanced atomic layer deposition (PEALD) of TiO_2/Al_2O_3 nanolaminates on silicon(100) and glass substrates were studied in order to discuss the growth mechanism and material properties of the films. We use the nanolaminate concept where each TiO_2/Al_2O_3 nanolaminate incorporates a certain number of Al_2O_3 partial-monolayers (between 10 to 90) during 2700 total reaction cycles of TiO_2 under temperature of 250ºC [1]. TiO_2/Al_2O_3 films were deposited by a TFS-200 ALD system from Beneq. TMA and TTIP were used as metallic precursors, while H_2O or O_2 plasma were used as ligand. The growth mechanisms and fundamental properties of the TiO_2/Al_2O_3 nanolaminates were inferred from measurements of the film thickness, chemical composition, microstructure and morphology. In addition, some optical and mechanical characteristics were determined and correlated with fundamental properties. Results evidenced that the model proposed for thermal ALD TiO_2/Al_2O_3 nanolaminate is valid for PEALD, however it was necessary a higher number of Al_2O_3 layers for stop the TiO_2 crystallinity. This allows obtaining a nanolaminate with improved properties in comparison with thermal ALD, as for example higher transmittance, lower refractive index (near the value of 3.2 eV), low resistivity, and higher hardness and young modulus. These properties are interesting for sensing application, such as UV detection.

[1] J. Azadmanjiri, C. C. Berndt, J. Wang, A. Kapoor, V. K. Srivastava, C. Wen, J. Mater. Chem. A 2 (2014) 3695–3708

[2] G. E. Testoni, W. Chiappim, R. S. Pessoa, M. A. Fraga, W. Miyakawa, K. K. Sakane, N. K. A. M. Galvão, L. V. Santos, H. S. Maciel. Journal of Physics D: Applied Physics, 49 (2016) 375301.

4:15pm **EM-MoA-12 Texture Control of ALD $PbTiO_3$ and $PbTi_xZr_{1-x}O_3$ Films by Hot Chuck and Rapid Thermal Annealing***, **Nicholas A. Strnad**,* University of Maryland*; D Potrepka, J Pulskamp,* U.S. Army Research Laboratory*; Y Liu, J Jones,* North Carolina State University*; R Phaneuf,* University of Maryland*; R Polcawich,* U.S. Army Research Laboratory

$PbTi_xZr_{1-x}O_3$ (PZT) is a perovskite ferroelectric material that is widely studied for its high dielectric constant and piezoelectric coefficients. Thin-film PZT has found several commercial uses, namely ink-jet print heads, ferroelectric random access memory (FRAM), MEMS gyroscopes, and more recently PZT-MEMS based speakers. Niche technological applications include MEMS resonators, actuators, and transducers. Thin-film PZT is currently deposited by primarily 2-dimensional (2-D) deposition techniques such as sol-gel, sputtering, and MOCVD. Thin-film PZT-based devices could benefit greatly from an atomic layer deposition (ALD) PZT process capable of transitioning traditionally 2-D architectures to 3-dimensional (3-D) architectures utilizing etched high aspect-ratio sidewalls to greatly enhance areal density especially for actuator technologies. The literature on PZT deposited by ALD is sparse and falls short of providing industry with an off-the-shelf solution. Additionally, there is little effort dedicated to controlling the texture of ALD PZT films, which is a desired component for many of the aforementioned technologies. Here we explore several techniques for controlling the texture of ALD PZT by depositing nucleation seed layers. First, we attempt to deposit 1-3nm of ALD grown TiO_x followed by 1-5nm ALD grown PbO_x and anneal in a PZT sputter chamber which has a PbO_x partial pressure. The PbO_x is expected to react with the TiO_x to form $PbTiO_3$ (PTO), but will be self-limited to what can be chemically incorporated because excess lead oxide will boil off the surface with the chuck maintained at 600° C or hotter. Second, we deposit 1-5nm of ALD grown TiO_x and anneal in an RTA that is expected to have a small PbO_x partial pressure due to re-deposition of lead oxide from prior processing of chemical solution deposited PZT films onto a quartz glass liner that is within 1 cm of the wafer surface. Third, as a control we deposit 40nm of PTO by sol-gel with 30% lead excess which crystallizes primarily in the 100/001 orientations following post-deposition anneal. Each of the ALD PZT films are deposited in an amorphous state and later crystallized by rapid thermal anneal in an O_2 atmosphere. To further evaluate the contribution of the nucleation layers to the texture, sol-gel PZT films are deposited in the first and second cases to be analyzed alongside the ALD PZT films. The films are characterized primarily by spectroscopic ellipsometry for film thickness, scanning electron microscopy for film thickness and microstructure, x-ray diffraction for phase identification and texture, and for select samples STEM with EDS for detailed structure and chemical analysis.

4:30pm **EM-MoA-13 Optical and Electrical Properties of $Ti_xSi_{(1-x)}O_2$ Films Prepared by ALD***, **Lenka Zajickova**, P Ondracka, D Necas,* Masaryk University, Czech Republic*; M Elias,* CEITEC, Brno University of Technology, Czech Republic*; J Vida,* Masaryk University, Czech Republic*; D Holec,* Montanuniversitat Leoben*; A Goullet,* University of Nantes

The mixed TiO_2-SiO_2 oxides have multiple possible optical applications with demonstrated use in waveguides, laser mirrors and rugate filters. They are also considered as an alternative dielectric for high-k applications and they attracted considerable attention in the area of photocatalysis because they are more active than pure TiO_2. $Ti_xSi_{(1-x)}O_2$ were deposited on Si substrate by plasma enhanced atomic layer deposition using tetrakis(dimethylamido)titanium and tris(dimethylamino)silane precursors for Ti and Si, respectively. The overall stoichiometry of the final thin film was varied by changing the relative number of TiO_2 and SiO_2 cycles as 1:1, 2:1, 1:2 and 3:1. The chemical bonding in the films was confirmed by X-ray photoelectron spectroscopy (XPS). Optical properties were determined in the wide spectral range from the ellipsometry (NIR-UV spectroscopic ellipsometer J. A. Woollam V-VASE, 0.6-6.4 eV, angles of incidence 60, 65, 70 and 75°) and reflectance (VUV spectrometer McPherson VUVAS 1000, 5.6–10.3 eV, near-normal incidence) measurements. The results on dielectric function and band gap were in good agreement with the density functional theory (DFT) predicted optical properties of amorphous $Ti_xSi_{(1-x)}O_2$ solid solutions. The electrical properties of the films were investigated in the MOS capacitor structures using a wafer probe station and the 4200 Keithley semiconductor parameter analyzer. The mixed oxide dielectric constant is deduced from the C-V curves measured at 1 MHz in accumulation regime whereas the film stability is assessed from the C-V loops recorded by accumulation (A) to inversion (I) and I to A. The dielectric layer insulating characteristics were assessed from the measured leakage current and breakdown voltage.

4:45pm **EM-MoA-14 Concerted Coating and Reduction for the Fabrication of Magnetic Fe_3O_4/TiO_2 Core-shell Nanoparticles***, **Sarai Garcia**, A López-Ortega, A Chuvilin, M Knez,* CIC nanoGUNE, Spain

Composite nanoscale materials are under intense investigation, opting for merging the functionalities of the constituting materials. Fe_2O_3-TiO_2 core-shell nanoparticles (NPs) are among the intensely investigated composite NPs for their application potential in a broad variety of fields, such as, sensing, selective separation, biomedicine, or photocatalysis [1,2]. The combination of a titanium dioxide (TiO_2) shell and a magnetic iron oxide core can provide added value to the composite by tuning the biocompatibility, stability and/or photocatalytic properties through the TiO_2 shell and at the same time, the possibility to use the materials for hyperthermia, imaging or controlled positioning through magnetic fields [3].

In this work, Fe_2O_3 nanoparticles are coated with TiO_2 and concertedly turned magnetite Fe_3O_4-TiO_2 core-shell NPs through atomic layer deposition (ALD) at moderate temperatures (Figure 1). The generated coatings prevent agglomeration of the nanoparticles and re-oxidation to γ-Fe_2O_3 even at high temperatures, allowing for the use of post-process annealing and thus crystallization of the amorphous TiO_2 to anatase. The occurring reduction of Fe_2O_3 to Fe_3O_4 is a function of the applied precursor and the processing temperature. This presentation will detail on our process and the characterization of the materials by means of X-ray diffraction (XRD), magnetometry, Energy Dispersive X-Ray analysis (EDX) and electron microscopy.

[1] M. Stefan *et al.*, "Synthesis and characterization of Fe_3O_4-TiO_2 core-shell nanoparticles," *J. Appl. Phys.*, vol. 116, no. 11, 2014.

[2] W. Wu, X. Xiao, S. Zhang, F. Ren, and C. Jiang, "Facile method to synthesize magnetic iron oxides/TiO_2 hybrid nanoparticles and their photodegradation application of methylene blue," *Nanoscale Res. Lett.*, vol. 6, pp. 1–15, 2011.

[3] S. Exhibit, C. Strobel, R. Herrmann, A. A. Torrano, and I. Hilger, "Biocompatibility of titanium dioxide nanoparticles for diagnostic and therapeutic purposes in personalized nanomedicine," pp. 1–17, 2013.

5:00pm **EM-MoA-15 Aluminum Nitride – From Amorphous to Highly Oriented Hexagonal Thin Films***, Z Chen, M Bosund, I Tuoriniemi, V Malinen, Z Zhu,* ***Emma Salmi****, K Härkönen,* Beneq Oy, Finland

Aluminum nitride (AlN) has a wide band gap, good thermal and chemical stability, thermal conductivity and interesting electro-acoustic properties. It is used in several applications, of which many depend on the crystalline structure of the material. Barrier, passivation and dielectric layers benefit from amorphous structures [1]. However, highly oriented crystalline films are needed for instance in optoelectronic and surface acoustic wave devices [2].

In this work the aim was to deposit AlN films with varying crystallinities to separately address the needs of different application areas. TMA and $AlCl_3$ were utilized as the metal precursors, while NH_3 or NH_3 plasma were used as the nitrogen source. The deposition temperatures were varied from 220 to 550°C.

PEALD AlN films were deposited at 220°C from TMA and NH_3 plasma in a Beneq TFS 200 ALD reactor. On a 200 mm wafer a uniformity of 1.7% was achieved. The films were amorphous and had a refractive index of 1.88.

Thermal ALD process from TMA and NH_3 was studied at 350–475°C with a Beneq P400 batch ALD reactor. Significant effect of the pulsing sequence on the growth characteristics and film properties was observed. With the optimized process at 350°C, a GPC of 1.37 Å/c and refractive index of 2.10 were measured. The bulk oxygen and carbon contents were 1.0 and 0.4 at.%. The films were polycrystalline with randomly oriented hexagonal structure, and the degree of crystallinity was increased with increasing deposition temperature (Figure 1).

The Beneq P400 batch ALD reactor is equipped for studying ALD processes at high temperatures. This enabled us to increase the temperature range of the thermal ALD $AlCl_3$–NH_3 process from the previously reported 500 up to 550°C [3,4]. Significant improvement on the film quality was observed with increasing deposition temperature. The GPC and refractive index increased from 0.67 to 0.76 Å/c and 1.99 to 2.06. Simultaneously the bulk oxygen and chloride impurity contents decreased from 3.2 to 2.5 and 1.8 to 0.7 at.%. Furthermore, these results were achieved with a uniformity of 2.5% on a batch set-up with a planar surface area of 20 000 cm^2. All the films were polycrystalline with highly oriented hexagonal [001] structure as the only observed peak was (002) (Figure 2).

[1] M. Bosund et al., Appl. Surf. Sci. 256 (2010) 7434-7437.

[2] G.F. Iriarte at al., Mater. Res. Bulletin 45 (2010) 1039-1045.

[3] K.-E. Elers et al, J. De Phys. IV France 5 (1995) C5-1021–C5-1027.

[4] V. Rontu, J. Vac. Sci. Technol. A 36 (2018) 021508.

5:15pm **EM-MoA-16 Purely Thermal Deposition of Polycrystalline Gallium Nitride Films at 400ºC***,* ***Sourish Banerjee****, S Dutta, A Aarnink, J Schmitz, D Gravesteijn, A Kovalgin,* University of Twente, Netherlands

In the field of III-V semiconductor materials, research is focused mostly on epitaxially grown films. Developing their polycrystalline counterparts (e.g., polycrystalline gallium nitride or poly-GaN) may lead to their more widespread adoption in application areas, such as in microelectronics and lighting. Unlike traditional epitaxy, atomic layer deposition (ALD) of poly-GaN films allows for less stringent growth requirements such as reduced temperatures, atomic-level thickness control and direct growth on a variety of substrates without the need of buffer layers.

The majority of reports on low temperature deposition of poly-GaN from trimethylgallium (TMG) and ammonia (NH_3) precursors mention an additional means of activation (e.g., plasma) to dissociate NH_3. This is done to increase the chemical activity of ammonia (by forming radicals) with the TMG-chemisorbed surface. However, in this work, we have used a different (radical-free) chemistry to deposit GaN films by a purely thermal route; i.e., without plasma or other radical-production means. Such a deposition approach can be beneficial, for example, in industrial-scale batch-type reactors where uniform radical delivery is a challenge.

We have utilized the strong adduct-forming chemistry of the Lewis-acid TMG and the Lewis-base NH_3 on the growth surface (Fig. 1). At the deposition temperature of 400ºC the TMG-NH_3 adduct dissociates into a Ga-NH_2-Ga linkage, thereby forming the first monolayer of GaN in a self-limiting fashion. Due to the reversible nature of this adduct formation, at optimal gas-pressure conditions, alternate pulses of TMG and NH_3 with in-between purges result in the efficient film growth. This pressure-dependency of adduct formation is revealed by in-situ monitoring the growth with spectroscopic ellipsometry (SE), which shows a strong dependence of the growth per cycle (GPC) with the NH_3 partial pressure (Fig. 2). Using this approach, we obtained GPC values as high as 0,045 nm/cycle.

The efficient removal of all methyl groups of TMG during GaN deposition in the adduct-assisted mechanism is revealed from the low carbon content (1 at. %) in the films, as obtained from depth profiled X-ray photoelectron spectroscopy (Fig. 3). The cross-section scanning electron microscope (SEM) image (Fig. 4) shows a 23-nm GaN film deposited on aluminium nitride (AlN). Grazing-angle X-ray diffraction (GIXRD) spectrum (Fig. 5) reveals that the GaN film is polycrystalline and has a wurtzitic structure.

In our presentation, the purely thermal radical-free deposition of poly-GaN films will be detailed: focussing on the growth mechanism, determining the ALD window, and presenting several film properties.

5:30pm **EM-MoA-17 ABC-type pulsing for group 13 nitrides***, P Rouf,* ***Henrik Pedersen****,* Linköping University, Sweden

The group 13 nitrides (13-Ns) are essential electronic device materials for present and future technologies. Thin film deposition of AlN and GaN are well explored by CVD at relatively high temperatures (800-1000°C). The high temperature aids epitaxial growth and ligand removal, rendering high crystalline quality films with low impurity levels. As 13-N CVD almost exclusively uses the trimethyl complexes of the group 13 metals, carbon is a major impurity with concentrations in the 10^{17} cm^{-3} range.

ALD is less explored for the 13-Ns but would open to topographically more advanced 13-N structures, higher control when depositing multilayer superlattice 13-N structures and possibly low deposition temperatures. A major challenge for ALD is the limitation in deposition temperature set, mainly by the thermal stability of the monolayers formed by the surface chemical reactions in the ALD cycle. The thermal stability of the group 13 precursors also limits the deposition temperature; $AlMe_3$ decomposes at about 330°C and previous studies have shown that the carbon content in the films increases rapidly when deposition temperature starts to approach the decomposition temperature [1]. The lower temperatures used in ALD compared to CVD hampers the crystalline quality and the removal of ligands leading to an increase in impurity levels, mainly carbon and oxygen, to the several atomic percentage levels.

Here we discuss the possibility to use the time-resolved precursor supply in ALD with an additional pulse between the precursor pulses, i.e. an ABC-type pulsing, to decrease impurities and increase crystalline quality. To improve the crystalline quality, we intentionally move out of the ALD temperature window and did time-resolved CVD of 13-Ns at 480°C, allowing thermal decomposition of the $13Me_3$ precursors. We then introduced a pulse of H_2 or N_2 gas or H_2-, N_2- or Ar plasma as B-pulse between the $13Me_3$ (A-pulse) and NH_3 (C-pulse) to study how it can aid the removal of ligands, as probed by the impurity levels in the deposited films. XPS measurements shows that the carbon content in AlN can be reduced from about 3 at. % to below 1 at. % (which is on the detection limit of XPS) by a H_2 gas or H_2 plasma as the B-pulse. H_2 gas as B-pulse also increases the GIXRD peak intensity, which is likely an effect of a higher crystalline quality, and the growth per cycle. Initial results do not show any improvement on the carbon content for N_2 plasmas as B-pulse in AlN deposition.

Financial support from the Swedish Foundation for Strategic Research (SSF RMA 15-0018) is gratefully acknowledged.

[1] H. Van Bui et al. ECS J. Sol. Stat. Sci. Technol. 2014, 3, P101-P106.

Emerging Materials
Room 107-109 - Session EM-TuA

Organic-Inorganic Hybrid Materials

Moderator: Virginia Wheeler, U.S. Naval Research Laboratory

1:30pm **EM-TuA-1 Simultaneous Enhancement of Toughness and Elimination of the UV Sensitivity of Kevlar with a Combined ALD/MPI Process***, **Itxasne Azpitarte**, M Knez,* CIC nanoGUNE, Spain

Kevlar® is among the most prominent high-strength polymers for a use in mechanically demanding applications, such as personal safety, sport equipment and aircrafts. In many of these applications Kevlar is exposed to UV radiation and/or moisture, which seriously affect its mechanical properties. Thus, strengthening or protection of Kevlar is of great interest. So far, the most efficient approaches resulted in heavy and rigid composite materials consisting of Kevlar fibers embedded in a resin [1]–[3].

Kevlar´s outstanding strength arises from the highly ordered crystalline structure formed during the extrusion of the polymer. Astonishingly, little attention has been paid to the possibility of enhancing the mechanical properties and stability via chemical post-processing of the polymer. In our previous work [4], we demonstrated that the thermal and UV sensitivity of Kevlar can be suppressed by infiltration of ZnO through Multiple Pulsed Infiltration (MPI). However, still only 90% of the modulus of toughness was retained in this way.

In this work, we present an extraordinary improvement of the properties of the fibers after applying a combined ALD/MPI process. Kevlar fibers have been infiltrated with ZnO and coated with Al_2O_3 in the same process. In this way, not only the loss of the modulus of toughness was suppressed, but the fibers even gained 10% of toughness. Simultaneously its sensitivity to UV-induced degradation was completely eliminated. This new processing strategy is a breakthrough in the improvement of Kevlar and promises further optimization with refinement of the processing conditions and precursors.

[1] J. R. Yeh, J. L. Teply, and A. Laboratories, "Compressive Response of Kevlar / Epoxy Composites," vol. 22, no. March 1988, pp. 245–257, 2015.

[2] a Mittelman and L. Roman, "Tensile properties of real unidirectional Kevlar / epoxy composites," vol. 21, no. 1, pp. 63–69, 1990.

[3] R. J. Morgan, C. Pruneda, and W. J. Steele, "The Relationship between the Physical Structure and the Microscopic Deformation and Failiure Processes of Poly(p-Phenylene Terephthalamide) Fibers," *J. Polym. Sci. Polym. Phys. Ed.*, vol. 21, pp. 1757–1783, 1983.

[4] I. Azpitarte *et al.*, "Suppressing the Thermal and Ultraviolet Sensitivity of Kevlar by Infiltration and Hybridization with ZnO," *Chem. Mater.*, vol. 29, no. 23, pp. 10068–10074, 2017.

1:45pm **EM-TuA-2 Mutual Synergistic Doping in Conductive Hybrid Materials Obtained after Vapor Phase Infiltration***, W Wang, I Azpitarte, **Mato Knez**,* CIC nanoGUNE, Spain

Hybrid materials are in most cases blends of inorganic and organic materials and are considered to be key for the next generation of materials research. The main goal while fabricating such materials is to bridge the worlds of polymers and ceramics, ideally uniting the most desirable properties within a singular material. Furthermore, in a well performing hybrid material the individual components will add value to their counterpart in a synergistic way.

In this work, an innovative approach towards creating flexible electronic materials will be presented. Rather than growing thin conformal films, the ALD process technology is applied to controllably infiltrate metals into polymeric substrates, which leads to novel strategies for obtaining conductive polymers. On the one hand, single precursor infiltration processes are applied to dope conductive polymers such as polyaniline or P3HT in a post polymerization process, opening the pathway to easier structuring of the polymer substrates and a more precise control of the doping levels. This is of great importance for those conductive polymers, which upon doping do not allow further shaping anymore due to dopant-induced brittleness.

On the other hand, a completely new concept for fabricating conductive polymers will be presented, which also shows a paradigm shift. Namely, the infiltration strategy with multiple precursors is applied to fabricate polymer-inorganic hybrid materials that are able to mutually dope each other in a synergistic way. The interaction of the semiconducting and the polymeric phase increases the conductivity of the hybrid material by up to 5 orders of magnitude in comparison to the conventionally doped polymer or the semiconductor. This strategy opens a new pathway to construct flexible conductive materials and enables thousands of new material combinations for the fabrication of flexible electronic materials.

2:00pm **EM-TuA-3 Infiltration Synthesis of ZnO in a Non-reactive Polymer Facilitated by Residual Solvent Molecules***, X Ye, J Kestell, K Kisslinger, M Liu,* Brookhaven National Laboratory*; R Grubbs,* Stony Brook University*; J Boscoboinik, **Chang-Yong Nam**,* Brookhaven National Laboratory

Infiltration synthesis is an atomic-layer-deposition (ALD)-derived organic–inorganic material hybridization technique that enables unique hybrid nanocomposites with improved material properties and inorganic nanostructures replicated from polymer templates. The process is typically perceived to be driven by the binding reaction between reactive chemical groups of polymers and infiltrating vapor-phase material precursors. In this work, we discover that residual solvent molecules from polymer processing can react with infiltrating precursors to enable the infiltration synthesis of metal oxides in a nonreactive polymer. The experimental investigation, combining in situ quartz crystal microgravimetry, polarization-modulated infrared reflection–absorption spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy, reveals that the ZnO infiltration synthesis in a nominally nonreactive, cross-linked SU-8 polymer is mediated by residual processing solvent cyclopentanone, a cyclic ketone whose Lewis-basic terminal carbonyl group can react with the infiltrating Lewis-acidic Zn precursor diethylzinc (DEZ). Additionally, we identify favorable roles of residual epoxy rings in the SU-8 film in further assisting the infiltration synthesis of ZnO. The discovered rationale not only improves the understanding of infiltration synthesis mechanism, but also potentially expands its application to more diverse polymer systems for the generation of unique functional organic–inorganic hybrids and inorganic nanostructures.

2:15pm **EM-TuA-4 Thermal Conductivity in Layer-engineered Inorganic-Organic Thin Films***, **Fabian Krahl**,* Aalto University, Finland*; A Giri, J Tomko,* University of Virginia*; T Tynell,* Aalto University, Finland*; P Hopkins,* University of Virginia*; M Karppinen,* Aalto University, Finland

The combined atomic/molecular layer deposition (ALD/MLD) offers unprecedented opportunities to design exciting layer-engineered film structures not readily achievable by any other fabrication technique. We utilize this to design hybrid inorganic-organic thin films structures that suppress the thermal conductivity of the inorganic component. Such thin films are desired for example for thermal barrier coatings and wearable thermoelectrics.

Our material system is the semiconducting ZnO matrix with thin benzene layers embedded within the the thicker oxide layers. In our previous works we already could show that a significant reduction in thermal conductivity can be achieved by introducing a superlattice, most likely caused by phonon scattering at the layer interfaces.[1,2] Now we extend our work towards irregular and gradient structures in which the layer thickness is not constant (as it is in regular superlattices), see Figure 1.[3] Our results show that the layer design is playing an important role and that a cleverly designed gradient structure can surpass the superlattices in regards to the suppression of thermal conductivity.

Our research extends the data for engineered hybrid thin films to gradient layered systems that have, to the best of our knowledge, not been provided before. We believe this approach is not limited to our present ZnO:benzene material system and hope it can help understanding the interaction of film design and properties in thin films.

[1] T. Tynell, A. Giri, J. Gaskins, P. E. Hopkins, P. Mele, K. Miyazaki, M. Karppinen, *J. Mater. Chem. A***2014**, *2*, 12150.

[2] Giri, J.-P. Niemelä, T. Tynell, J. T. Gaskins, B. F. Donovan, M. Karppinen, P. E. Hopkins, *Phys. Rev. B***2016**, *93*, 115310.

[3] F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins, M. Karppinen, *Adv. Mater. Interfaces*, in press (**2018**).

[4] J. Alvarez-Quintana, E. Martínez, E. Pérez-Tijerina, S. A. Pérez-García, J. Rodríguez-Viejo, *J. Appl. Phys.***2010**, *107*, 063713

2:30pm **EM-TuA-5 Reversible Trans-cis Photoisomerization of ALD/MLD-fabricated Azobenzene-based Inorganic-Organic Thin Films***, **Aida Khayyami**, M Karppinen,* Aalto University, Finland

We report the successful incorporation of photoresponsive azobenzene molecules through atomic/molecular layer deposition (ALD/MLD) in inorganic-organic thin films. Together with azobenzene-4, 4'-dicarboxylic acid as the organic precursor we use diethyl zinc (DEZ) as the inorganic precursor for our hybrid thin films of the (Zn-O-$C_{14}H_9N_2$-O_4-) $_k$ type. The fabrication route developed for the hybrid films was then combined with the diethylzinc/H_2O ALD process for ZnO in order to grow $[(ZnO)_m(Zn–O–C_{14}H_9N_2\text{-}O_4\text{-})_{k=1}]_n$ superlattice structures where single azobenzene layers are sandwiched between thin crystalline zinc oxide blocks. The ratio of the ALD-ZnO and MLD-(Zn-O-$C_{14}H_9N_2$-O_4-) cycles was varied between 199:1 and 1:1. The kinetics of the trans-cis-trans photoisomerization were studied by alternate exposures to UV radiation and visible light ($\lambda > 450$ nm). Our inorganic-organic hybrid and superlattice structures were found to be photoreactive upon 360 nm irradiation. This observation confirms that switching processes with photochromic compounds, such as azobenzene, can be implemented in inorganic-organic thin films prepared by the ALD/MLD technique. This underlines the exciting new possibilities provided by the ALD/MLD technique for preparing novel light-sensitive materials.

2:45pm **EM-TuA-6 Organic/Inorganic Nanocomposite Synthesis through Sequential Infiltration of 3D Printed Polymer Parts: A Microstructural Study**, ***David J. Mandia***, Argonne National Laboratory; *R Waldman,* University of Chicago; *P Kozak,* Argonne National Laboratory; *S Letourneau,* Boise State University; *G Sterbinsky, D Gosztola, L Ocola, A Yanguas-Gil, J Elam,* Argonne National Laboratory

The modification of polymer 3D printed parts using chemical vapor infiltration methods, such as sequential infiltration synthesis, can be used to impart novel functional properties to 3D printed parts. In this work, we describe the infiltration and characterization of 3D printed parts composed of polymers including poly(lactic acid) (PLA), poly(methyl methacrylate) (PMMA) and acrylonitrile butadiene styrene (ABS), with ZnO using diethyl zinc and water. This results in the formation of a hybrid organic/inorganic composite in the sub-surface region of the polymer whose thickness depends on processing conditions. Through a combination of X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and photoluminescence, we have studied the bonding environment, medium range order, and electronic properties of the resulting material. We discovered that through control of the purging step, growth can proceed in two different regimes, one in which the growth seems to be dictated by precursor molecules coordinating with reactive sites within the polymer, and another that is consistent with infused precursors reacting within the polymer itself. This results in a higher incorporation of inorganic material and a change in microstructure from a coordination environment characteristic of atomic-size inorganic cluster to denser, wurzite-like domains.

3:00pm **EM-TuA-7 Reactivity of Common ALD Precursors with OH/H_2O-containing Metal Organic Framework Materials**, ***Kui Tan,*** University of Texas at Dallas; *S Jensen,* Wake Forest University; *L Feng,* Texas A&M University; *H Wang,* Rutgers University; *J Klesko, R Rahman, J Cure, K Wei,* University of Texas at Dallas; *H Zhou,* Texas A&M University; *J Li,* Rutgers University; *T Thonhauser,* Wake Forest University; *Y Chabal,* University of Texas at Dallas

The ability to incorporate metal atoms into nanoporous materials such as metal organic frameworks (MOFs) in a well-controlled fashion provides new opportunities to prepare functionalized and modified materials for potential applications such as catalysis and gas separation. There are however new challenges that need to be overcome such as understanding the reaction mechanisms in order to develop structural and process optimization. MOFs possess three-dimensional structures, with complex pore architecture, leading to a number of possible processes (gas transport, adsorption and reaction) that are much more complex than on flat surfaces. To address these issues, we have combined *in-situ* infrared spectroscopy, X-ray-photoelectron spectroscopy and *ab initio* calculation to study the reaction of a number of common ALD precursors -- trimethylaluminium (TMA), diethylzinc (DEZ), titanium tetrachloride ($TiCl_4$)-- with in several Zr-MOFs containing hydroxyl (OH) and water (H_2O) groups. Differentiating reaction with OH and H_2O groups is particularly interesting since their reactivity highly depends on both the chemical and structural (i.e. sterics) environments. We find that the OH groups in the $Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4(OH)_x(OH_2)_y$ cluster node do not all react at similar rates (i.e., the reaction pathway and energetics are highly dependent on their location, accessibility and chemical environment). For different OH-containing MOFs without H_2O groups, the activation temperatures for the TMA reaction with bridge OH of Zr_6 clusters decrease with their node connectivity, and are 250°C, 150°C and 24°C for UiO-66-NH_2, Zr-abtc and MOF-808, respectively. Interestingly, the amine group in UiO-66-NH_2 is found to act as a catalytic active site by anchoring TMA molecules and facilitating their reaction with nearby hydroxyl groups, which is not observed in un-functionalized UiO-66. This synergistic effect between -NH_2 and -OH is fully elucidated by first-principles calculations. In addition, we find that TMA easily reacts with water adsorbed on the external surfaces of wet MOFs crystals at room temperature, forming a thick Al_2O_3 blocking layer on the periphery of MOFs crystals. These findings provide a basis for the design and synthesis of new MOFs structures requiring ALD for new applications.

3:15pm **EM-TuA-8 Atomic/Molecular Layer Deposition of Inorganic-Organic Carboxylate Network Thin Films for Possible Sensing Applications**, ***Jenna Penttinen***, *M Nisula, M Karppinen,* Aalto University, Finland

We introduce novel atomic/molecular layer deposition (ALD/MLD) processes for the fabrication of crystalline inorganic-organic coordination network thin films with different s-block elements and different aromatic polycarboxylates. The deposition processes fulfill the basic principles of ALD/MLD-type growth including the sequential self-saturated gas-surface reactions and atomic/molecular-level control of the film thickness, and yield crystalline thin films in a wide deposition temperature range. We have investigated the stability of the films in heat and humidity treatments to verify that some of the films reversibly absorb water molecules forming well-defined crystalline water-derivative phases. This suggests that the materials could be utilized e.g. for gas storage and sensing applications. Also interestingly, for some of our as-deposited crystalline thin-film materials there are no bulk structures reported in literature. Our work thus underlines the strength of the ALD/MLD technique in discovering new exciting coordination network thin-film materials that may ultimately be potential material candidates for the next-generation application in, e.g., electronics, sensors, and other high-technology products.

Emerging Materials
Room Premier Ballroom - Session EM-TuP
Emerging Materials Poster Session

EM-TuP-1 Structural and Optical Properties of Luminescent Copper (I) Chloride Thin Films Deposited by ALD, ***Tomáš Homola**, R Krumpolec, D Cameron, O Caha, J Humlíček,* Masaryk University, Czech Republic*; R Zazpe, J Přikryl, J Macák,* University of Pardubice, Czech Republic

Zinc blende-structure g-copper (I) chloride is a wide, direct bandgap semiconductor with the potential for applications in UV optoelectronics. We report on the structural, optical and photoluminescent properties of CuCl thin films deposited by atomic layer deposition. The CuCl films were deposited at a reaction temperature of 125 °C from [bis(trimethylsilyl)acetylene] (hexafluoroacetylacetonato)copper(I) and pyridine hydrochloride precursors with pulsing times 2 and 6 s with corresponding purging times 4 and 6 s respectively. The CuCl growth was deposited on various substrates: amorphous soda-lime glass, amorphous quartz glass, crystalline silicon and crystalline sapphire of different orientations. The deposited coatings at 100, 200, 500 and 1000 ALD cycles were studied by XPS, XRD, AFM, optical reflectance and photoluminescence. We also investigated the effectiveness of a thin capping layer of aluminium oxide against degradation of the CuCl by atmospheric. The presence of CuCl was confirmed by the x-ray diffraction and photoluminescence measurement which showed a strong signal at approx. 3.25 eV characteristic of the excitonic emission. The presence of crystalline CuCl was strongly influenced by the substrate and the best crystallinity was found on quartz glass, whereas silicon wafers showed no evidence of CuCl crystals in the deposited films. Moreover we also showed that quick optical reflectance measurement can be used for fast and reliable detection of the presence of CuCl crystals.

EM-TuP-2 Wafer-scale Fabrication and Optoelectrical Application of Organic-inorganic Perovskite Single Crystal Arrays, ***Lynn Lee**, M Sung,* Hanyang University, Republic of Korea

Organic-inorganic hybrid perovskites, especially $CH_3NH_3PbX_3$ (X=Cl, Br, I) have received great attention due to their outstanding light-harvesting properties as well as their low-cost device fabrication process. Their superior optoelectrical properties lead to the exceptional device performances of these materials in various applications such as solar cells, LEDs, and photodetectors. Typically, the quality of the crystal is a well-known factor to decide the efficiency of those optoelectronic applications with long carrier diffusion length and high mobility. However, since a thin film of a single crystal cannot be obtained by a typical film fabrication method, films made by most of the manufacturing methods suffer from low crystallinity issue. For these reasons, fabrication of single crystalline perovskite thin film is required for high-efficiency device applications.

Here, we fabricate the wafer-scale perovskite single crystal arrays in thin film form and characterize the crystallinity of the perovskite thin film by X-ray diffraction (XRD) and selected area electron diffraction (SAED). Also, the morphology of perovskite crystals was observed using optical microscopy (OM) and scanning electron microscopy (SEM). Furthermore, the perovskite patterned thin films are applied in lateral solar cell applications. The average efficiency of the perovskite lateral solar cell in low light intensity is over 4%, which are the world-top efficiency in lateral perovskite solar cell field as far. From this work, the probability of the perovskite single crystal array is successfully demonstrated.

EM-TuP-3 Organic-inorganic Hybrid Optoelectronic Device by Atomic Layer Infiltration, ***Yeongeun Bak**, M Sung,* Hanyang University, Republic of Korea

Hybrid organic-inorganic solar cell have emerged as a remarkable new alternative energy source over the past few years to solve the global energy problems. The sun is sustainable, reliable and long-term supply of energy, in contrast to conventional resources such as fossil fuels. Silicon is the most widely used as material of solar cell because of its high efficiency, but it has limits; expensive manufacturing cost and limitation of application to flexible or transparent devices. So, alternative types of solar cells are also being researched, Sb_2S_3 solar cell is up-rising candidate for next generation solar cells overcoming the above disadvantage of Si solar cell. The problem of commercialization of Sb_2S_3 solar cell is lower efficiency than Si solar cells, so there were previous studies about interfacial engineering have been proceeding for solving the problems.

We studied new organic-inorganic material nickel-4-mercaptophenol (Ni-4MP), as an interfacial engineering material into Sb_2S_3-hole transport material interface. Ni-4MP thin film is deposited using atomic layer deposition method. For infiltrate precursors into FTO/mp-TiO2/Sb_2S_3 structure, exposing procedure is added. The reference cell structure is FTO/mp-TiO2/Sb_2S_3/P3HT/Au. We measured the photo conversion efficiency using solar simulator with source-meter for comparing two samples. And then we observed impedance measurement with variation of voltage for confirming the effect of Ni-4MP on Sb_2S_3 solar cell. As a result, electron lifetime calculated from this measurement proof the longer lifetime of electron after insert Ni-4MP as interfacial engineering material.

EM-TuP-4 A Common Source/Drain Metallization Scheme for (In)GaAs and Ge Channel Materials Featuring Low Contact Resistances, ***Szu-Hung Chen**,* National Nano Device Laboratories (NDL), NARL, Republic of China*; K Chen, Y Chen,* College of Photonics, National Chiao-Tung University, Republic of China*; C Chu, G Luo,* National Nano Device Laboratories (NDL), NARL, Republic of China*; C Lin,* College of Photonics, National Chiao-Tung University, Republic of China

Pursing of the miniaturization of Si-based logic transistors is approaching it's fundamental limits in aspects of geometric scaling, enhancement of intrinsic carrier transport efficiency as well as reduction of parasitic components. Serial extrinsic S/D resistance can seriously degrade the output current of the transistor and constrain it from low-voltage operation. As the transistor channel length (Lg) shrinks, the device's intrinsic channel resistance decreases. Consequently, the parasitic source/drain resistance (R_{sd}) dominates and plays key role in determining the overall device output characteristics, particularly when the technology node is beyond 7 nm and smaller. Despite the stringent challenges in reducing R_{sd}, CMOS technology also requires both n- and p-type transistors in a single chip for various logic functions in integrated circuits. Si is the channel material of current n-/p-type transistors used for industrial mass production. However, due to the potential of incorporating alternative channel materials for future-generation CMOS, n-type and p-type channels may be different materials to maximize the performance. For example, InGaAs, possessing high electron mobility, is used in n-type channel devices and Ge, possessing high hole mobility, is used in p-type channel device, respectively, in an attempt to achieve the best combined performance in CMOS. In such a scheme, the complexity of processing heterogeneous CMOS dramatically increases. From this point of view, it is of great interest and is mandatory to reduce the process complexity, especially in the step of source/drain contact metallization. In this work, targeting the future nano-device application, a single metallization scheme for n-/p-type channel transistors has been developed to reduce the cost of the CMOS manufacturing. W/TiN/Ti multilayer structure is adopted to form metal/$In_{0.53}Ga_{0.47}As$ and metal/Ge contacts. Both contact structures show specific contact resistance of <3E-7 Ωcm^2 by CTLM (circular transmission line model) analysis. However, the interracial relations are distinct as evidenced by material analysis. The promising results show that the developed technology is of great potential for application in future of nano CMOS technology which requires heterogeneous n-/p-channels.

EM-TuP-5 Ruthenium Precursors - Properties and ALD Application, ***Andreas Wilk**, O Briel, D Zeng, A Frey, A Rivas Nass, W Schorn,* Umicore AG & Co. KG, Germany

Umicore has its roots in precious metal chemistry and has significant expertise in making new MOCVD and ALD precursors available at high manufacturing volumes. The necessary scale up skills include substantial supply chain involvement, solid chemical background, purification competence, trace metal analytical capabilities and significant packaging knowhow.

Besides the established cobalt and tungsten precursor portfolio we have established new chemistries for ruthenium based compounds as ruthenium tungsten and cobalt are considered by several chipmakers at 5nm and below for upcoming applications.

Ruthenium is a precious metal with interesting chemical, crystallographic and electronic properties. This makes ruthenium chemistry including the related precursors very interesting for chipmakers for logic as well as memory applications. In our poster we will introduce established and new precursors with a variety of ligands currently considered and review their relevant physical and analytical properties for interesting metal and oxide ALD industry applications including the 5 nm node and below.

EM-TuP-6 Magnetic and Electrical Performance of Atomic Layer Deposited Nanostructures*, **Aile Tamm**, K Kalam, M Mikkor, H Seemen, A Šutka, U Joost, M Rähn, K Kukli,* University of Tartu, Estonia*; J Link, R Stern,* National Institute of Chemical Physics and Biophysics*; H Castán, S Dueñas,* University of Valladolid

The synthesis of multiferroic materials is of relevance while developing the next generation electronic and spintronic devices [1]. Theoretically, several materials could demonstrate saturating and remnant polarization in both electric and magnetic fields, but it is challenging to actually synthesize thin films which demonstrate multiferroic behaviour, because the physical performance of the materials may considerably depend on their synthesis routes. In this study we compare the nanostructures containing nanoparticles $CoFe_2O_4$ or $MnFe_2O_4$ covered by high-k films by ALD with nanolaminate films consisting of high-permittivity oxides (ZrO_2, Er_2O_3) and magnetic materials (Bi_2O_3, Fe_2O_3, Co_3O_4) grown by ALD. Nanolaminate films could be uniformly deposited into three dimensional stacked substrates using the same cycle times otherwise suited to the uniform coverage of planar substrates. The morphology, crystalline phases and composition of nanostructures were described. Those nanostructures promoted both charge polarization and saturative magnetization. Promising results in terms of the simultaneous appearance of the internal magnetization and certain electrical charge polarization were demonstrated in some planar nanostructures. Further electrical and magnetic modelling and analysis will be needed in order to elaborate the phenomenon and optimize the material structure for the magnetoelectric performance.

Acknowledgements

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EM-TuP-7 $HfZrO_2$ Deposited by ALD using TEMAH and ZrCMMM Precursors*, **Ronald Grundbacher**,* IBM Research – Zurich, Switzerland*; Y Ju,* ETH Zurich, Switzerland*; F Eltes,* IBM Research – Zurich, Switzerland*; X Chen,* ETH Zurich, Switzerland

Hafnium zirconium oxide ($HfZrO_2$) with thickness on the order of a few nanometers to tens of nanometers is of interest as a high-k dielectric material that is integrated into compound semiconductor and CMOS devices, nanowire-based devices, and nanostructured devices based upon novel materials. The ferroelectric properties of $HfZrO_2$ are of interest for low-power steep-slope transistor applications and nonvolatile memory. The requirements of the $HfZrO_2$ that is integrated into the above mentioned devices include low concentration of impurities, low interface and bulk trap densities, low leakage current, and often, low temperature deposition due to a limited thermal budget. The characteristics of $HfZrO_2$ deposited by atomic layer deposition (ALD) has been investigated with the above requirements in mind, and deposition parameters have been determined to optimize the Hf/Zr ratio.

Hafnium zirconium oxide thin films were deposited on silicon wafers by atomic layer deposition using tetrakis(ethylmethylamino)hafnium (TEMAH) and bis(methyl-η^5–cyclopentadienyl)methoxymethylzirconium (ZrCMMM) precursors and either oxygen plasma or ozone. Oxygen plasma and ozone conditions, Hf to Zr pulse ratio and sequencing, as well as deposition temperature (250ºC to 350ºC), were varied, and their effects on the $HfZrO_2$ thin films were investigated. The properties of the ALD deposited films were comparatively characterized. The $HfZrO_2$ thin films were characterized by ellipsometry to determine the thickness (growth rate) and dielectric constant, and they were characterized by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectorscopy (RBS) to determine the hafnium and zirconium content. Atomic force microscopy (AFM) was used to characterize surface roughness and piezoresponse force microscopy (PFM) was used to determine the ferroelectric nature of the $HfZrO_2$ films.

EM-TuP-8 Non-destructive And Precise Control Of Electronic Properties via N-Doping Method with Atomic Layer Deposition.*, **Jong Chan Kim**,* Hanyang University, Repubic of Korea*; M Sung,* Hanyang University, Republic of Korea

For variety of usage, graphene must be under processed its Fermi level and carrier concentration. In this approach introduced n-doping technique with atomic layer deposition(ALD) of Zinc oxide. Precise even quite simple and, the produced ZnO thin film on graphene are uniform, conformal, of good quality with a low pinhole density, besides thickness control of 1 Å resolution available. Evaluation of material properties performed which characterization of graphene transistor at the point of carrier density, doping state and Dirac point as a function of the thin film thickness. Our achievement is not only electronic properties’ progress, but also stable device performance has gotten. It is caused from ZnO film did a role of effective barrier against air-borne water and oxygen on the graphene. Additionally, ZnO ALD enhanced too to the other promising 2D materials like MoS_2 and WSe_2 those are candidates to promote electron mobility.

EM-TuP-9 Curvature-Dependent Surface Potentials of Zincone Films Grown by Molecular Layer Deposition*, J Lee, **Yun Yeong Lee**,* Sookmyung Women's University, Republic of Korea

Molecular layer deposition (MLD) is a method for obtaining conformal ultrathin organic films using vapor-phase organic precursors, while their composition and thickness can be controlled at the molecular level. This process is based on self-saturating reactions between the precursors and the substrate surface. Also, in comparison with solution-based technique, it allows epitaxial growth of molecular layer on substrate and is especially good for surface reaction or coating of nanostructures such as nanopore, nanobead, nanowire array and so on.

In this study, we fabricated organic-inorganic zincone polymeric films on surfaces with various curvatures through coupling reactions between diethyl zinc (DEZ) and 2-Butyne-1,4-diol (BYDO) as inorganic and organic precursors, respectively, by molecular layer deposition. Using ellipsometry and transmission electron microscope (TEM), we confirmed the different growth behavior of zincone films grown on curvature substrates with different ratio. And, we investigated their curvature-dependent surface potentials by performing *ex situ* analysis using scanning kelvin probe microscopy (SKPM). Furthermore, their molecular geometries and energies on substrates with various curvatures were predicted by performing density functional theory (DFT) calculations.

EM-TuP-10 Photo-switchable Behavior of Azobenzene-containing Polyamide Films Grown by Molecular Layer Deposition*, J Lee, **Hyemi Lee**,* Sookmyung Women's University, Republic of Korea

Photo-sensitive polymer film has been attracted in the field of material science including biological system and optical devices which are sensitive on the change of surface topology. Recently, azo compound (R-N=N-R’), as one of the photo-induced reversible transformation unit, has been highlighted in the research related photo-sensitive polymer film including surface science, artificial muscle, biological and optical application, because light used as external triggers for inducing surface transformation is manageable to control without modification of nano-structures and environment concerns.

In this study, we fabricated photo-reversible polyamide film based on coupling reactions between azobenzene-4, 4’-dicarbonyl dichloride (Azo) and one of two diamine compounds, which are phenylenediamine (PDA) and hexamethylenediamine (HDA) by molecular layer deposition through self-limiting surface reaction. And, we investigated the photo-induced reversible transformation of azobenzene-containing polyamide thin film. In situ Fourier Transform Infrared (FTIR) measurement was used to monitor the growth of polyamide film, and the light-induced transformation was characterized by UV-vis spectroscopy.

EM-TuP-11 Phase Selective, Low Temperature Growth of TiO_2 by Atomic Layer Epitaxy*, **Virginia Wheeler**, D Boris, S Qadri, J Freitas, S Walton, C Eddy, Jr.,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) of TiO_2 has been widely explored in recent years due to its promise in non-volatile resistive switches, high-k gate dielectrics, solar cell, and photocatalytic applications. This method has become increasingly useful as device dimensions are reduced and non-planar complexity is increased. Traditionally, the low ALD growth temperature (Tg) yields amorphous films. To facilitate epitaxial films, many have investigated plasma, laser or photon, or electron enhanced ALD processes. Specifically for TiO_2, it would be beneficial to selectively grow epitaxial anatase or rutile phases in order to tailor properties for the required application. Typically, TiO_2 phase selectively is attained by varying the underlying substrate, Ti and/or oxidation precursor, or growth temperature. In this work, we demonstrate high quality epitaxial TiO_2 films at low temperatures and phase selectively by adjusting plasma gas composition, pressure and Tg.

A Veeco Fiji G2 reactor was used to deposit TiO_2 films on different sapphire orientations (c-, m-, a-) with tetrakis(dimethylamido)titanium (TDMAT) and either Ar/O_2 or pure O_2 plasma at 100-350°C. Previous reports indicate that tuning the ion energy, specifically through substrate biasing, can influence TiO_2 film crystallinity and phase [1]. The high pumping speed and large gas flow range available in the system provides a wide variation in operating pressures (7-100's mTorr), which effectively allows tuning of plasma characteristics. Operating at relatively low pressures (9-21mTorr) resulted in a significant flux ($0.5\text{-}1.5\times10^{19}$ $m^{-2}s^{-1}$) of very energetic ions (30-50eV); both the flux and energy decrease as the pressure is increased. The low pressure conditions yield high-quality epitaxial films at all temperatures, which differs from previous reports using these specific precursors [2,3] likely due to the plasma conditions.

Gas composition during the plasma step also had a substantial effect on growth rate, TiO_2 phase, and strain. At $T_g < 300°C$, the growth rate was increased from 0.5 to 0.7 Å /cycle by switching from Ar/O_2 to pure O_2. Additionally, an O_2 plasma produced only rutile TiO_2 films, with less strain, independent of growth temperature or underlying substrate orientation. In contrast, films deposited with an Ar/O_2 plasma show a phase dependence on temperature and substrate. Films on c-plane Al_2O_3 go from anatase at Tg below 200°C to rutile above 300°C. The films on m-plane Al_2O_3 are rutile independent of temperature.

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EM-TuP-12 ALD Deposited Thin Films as Model Electrodes: A Case Study of the Synergistic Effect in Fe_2O_3-SnO_2

J Kint, F Mattelaer, ***Christophe Detavernier,*** Ghent University, Belgium

Li-ion batteries are the current state of the art energy storage devices. They have been around since 1991, yet there still is room for improvement. On the anode side, specific capacities are relatively low. High capacity storage mechanisms (conversion, alloying) are gaining attention. However, these reactions impose strain on the material, leading to pulverization, contact loss, SEI formation and poor kinetics. However, synergistic effects were reported when two of these materials are combined.

Since electrodes are complex systems, we used atomic layer deposition to deposit model electrodes. This approach avoids the need for binders or additives and ensures simple, 1-dimensional Li^+-diffusion pathways. The self-limiting and digital nature of ALD ensures optimal control over the thickness and stoichiometry of the mixed oxides. Furthermore, it enables control of the degree of intermixing of the Fe_2O_3 and SnO_2 at the atomic scale. Here, films of pure Fe_2O_3, pure SnO_2, atomically intermixed Fe_2O_3-SnO_2 and a Fe_2O_3/SnO_2 nanolaminate were deposited with ALD and evaluated as anodes.

Although Li-alloying of SnO_2 delivers a huge capacity, undesirable island formation occurs. During lithiation of the intermixed Fe_2O_3-SnO_2, the conversion of Fe_2O_3 still occurs, yet the conversion and subsequent Li-alloying of SnO_2 is no longer present. Instead, another reaction occurs around 0.9V vs Li^+/Li which has no analogon in either pure SnO_2 or Fe_2O_3. Therefore it is hypothesized that it is a reaction of Li^+ with the $Fe_xSn_yO_z$ ternary oxide. Although the mix of these oxides shows no alloying of Sn, it ensures a better cycle life of the material, as the island formation caused by the alloying is avoided. This can be seen from the cyclability test, as the capacity of the mixed material is more stable than the SnO_2. From a kinetics point of view, the fully intermixed material compares well to the Fe_2O_3, especially at high currents.

For the nanolaminate we can also discern abovementioned reactions, as the interfaces between the oxides give rise to the peaks associated with those for the mixed material. Those corresponding with the conversion and subsequent alloying of SnO_2 are also clearly present. This entails that, although the nanolaminate provides a large capacity, the alloying of Sn still occurs and causes great stress and loss of contact, as can be seen from the SEM image after cycling the nanolaminate for a mere 50 cycles. This results in discrete capacity losses during cycling.

We used ALD to prove that in order to maximize the synergistic effect for Fe_2O_3/SnO_2, an atomically intermixed material is preferred over a nanolaminated system with interfaces between the oxides.

ALD Applications
Room 107-109 - Session AA3+AF+EM-WeM

AA+AF+EM

Moderator: Iian Buchanan, Versum Materials, UK

8:00am **AA3+AF+EM-WeM-1 Fabrication of TiO_2 Interconnected Nanotubes by ALD and Synthesis of g-C_3N_4/Au/TiO_2 Heterostructure for Photocatalytic Water Splitting***, **Li-Chen Wang**, L Tsai, C Liu, T Perng,* National Tsing Hua University, Republic of China

Recently, the catalysis science has ascended to a new horizon due to the advent of novel nanotechnologies such as atomic layer deposition (ALD) with the capability of fabricating a marvelous panoply of nanomaterials. The sequential and self-limiting gas-solid surface reactions of the ALD process enable to deposit extremely conformal and ultrathin film on a wide variety of templates, favoring the innovative design of various nanostructured photocatalysts. Herein, we report a controllable fabrication of a hybrid photocatalyst comprising graphitic carbon nitride (g-C_3N_4), Au nanoparticles, and TiO_2 hollow fibers for photocatalytic water splitting. Titanium tetrachloride ($TiCl_4$) and H_2O were used as precursors for the ALD process to uniformly deposit a thickness-controllable TiO_2 thin film on hollow polysulfone fibers (PSFs). In order to minimize the e^--h^+ pair recombination, the TiO_2 hollow fibers were further decorated with Au nanoparticles by chemical reduction and then coated with a g-C_3N_4 nanolayer by pyrolysis of urea at a certain elevated temperature. For comparison, Au/TiO_2 hollow fibers and Au/g-C_3N_4 nanosheets were also prepared and individually used as photocatalysts for water splitting. It was demonstrated that the photocatalytic efficiency of the g-C_3N_4/Au/TiO_2 heterostructure could be influenced by the thickness of the TiO_2 thin film which can be tailored by the ALD cycle number. TiO_2 with perfect conformality on the porous PSF template also offers a large surface area of the hybrid catalyst and efficient trapping of the reflected photons within the interconnected nanotubes of the hollow fibers. More importantly, the surface plasmon resonance (SPR) effect of Au nanoparticles and the g-C_3N_4/Au/TiO_2 heterostructure that could effectively increase the separation of e^--h^+ pairs further enhance the photocatalytic efficiency of g-C_3N_4/Au/TiO_2 for water splitting when compared to those of Au/TiO_2 and Au/g-C_3N_4.

8:15am **AA3+AF+EM-WeM-2 Nano-energetic Materials Fabricated by Atomic/Molecular Layer Deposition***, **Hao Feng**,* Xi'an Modern Chemsitry Research Institute, China

As key components to improve energy densities, metal nanoparticle based energetic materials are widely used in many energetic systems, for example, as additives for propellants and explosives. Metal nanoparticle based energetic materials have fairly large surface areas and are extremely reactive. Proper surface modification improves the safety and stability of these materials and may also enhance their energy releases. By applying atomic layer deposition (ALD) or molecular layer deposition (MLD), surfaces properties of the metal nanoparticles can be dramatically changed and their energy release patterns can be effectively tuned at minimum losses of the energy densities.

Zr nanopowder is a very promising high energy metal fuel. However, this material is extremely sensitive to electrostatic discharges, which greatly jeopardizes its applications. By applying ALD/MLD surface modification, metallic Zr nanoparticles can be encapsulated by uniform layers of metal oxides, polymers, or carbon. The thicknesses of the encapsulation layers can be precisely controlled. The electrostatic sensitivity of Zr nanoparticles can be tuned in a wide range by varying the type and thickness of the ALD coating, which significantly enhances the safety in handling, storage, and utilization of this high energy material.

Metal nanoparticle based thermite materials feature very exothermic solid-state redox reactions. However, reaction rates of traditional thermite mixtures are limited by reactant diffusion velocities. Core-shell structured nanothermite materials can be synthesized by depositing certain types of metal oxides (oxidizers) on Al nanoparticles. The oxidizer layers deposited on the Al nanoparticles are conformal and their thicknesses can be precisely controlled by adjusting the number of ALD cycle. Reaction rates of the core–shell structured nanothermites synthesized by ALD are several times faster than the mixture of nanopowders. The enhanced reaction rate is ascribed to the intimate fuel-oxidizer contact as a result of the exquisite core–shell nanostructure and excellent conformity of the oxidizer shells.

8:30am **AA3+AF+EM-WeM-3 Atomic Layer Deposition of Alumina on Lactose Particles for Modified Release: Effect of Co-reactants and Substrate Crystallinity***, **Damiano La Zara**,* Delft University of Technology, Netherlands*; D Zhang, M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden*; J van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) is an established technique for the synthesis of thin films for various applications ranging from semiconductors to energy storage devices. Recently, it has been gaining attention in the pharmaceutical field to modify the particle properties, for example the drug release. Compared to the conventional methods of drug particle coating, ALD has a number of advantages: control over the amount of deposited material, conformality, and its solventless nature. A few studies about ALD of metal oxides, including Al_2O_3, TiO_2 and ZnO, on acetaminophen, lactose and budesonide particles showed that the deposition of nanoshells can effectively slow down the drug release. However, the dependence of the film growth on pharmaceutical particles on the ALD operating conditions has not yet been investigated. Furthermore, the relationship between the properties of the coating (e.g, uniformity, conformality) and the dissolution behaviour of the resulting core-shell structures is not clear. Therefore, as the dissolution profile strongly depends on the coating quality, understanding how process parameters (e.g., number of cycles, co-reactants and substrate surface) affect the coating uniformity and conformality is crucial.

In this work, we study the effect of co-reactants, namely H_2O and O_3, on the Al_2O_3 growth on two kinds of lactose particles (i.e., fully crystalline lactose and crystalline lactose with micronization-induced amorphous surfaces) and evaluate the dissolution behaviour. The ALD process is carried out at ambient conditions in a fluidized bed reactor for a low number of cycles (i.e., from 4 to 14) using trimethylaluminum (TMA) as a metal precursor. Time-of-flight secondary ion mass spectrometry and Transmission Electron Microscopy (TEM) show that TMA/O_3 ALD on crystalline lactose particles offers greatly improved control over the coating uniformity and conformality compared to TMA/H_2O ALD. In fact, by causing severe agglomeration of the particles, water deteriorates the fluidization quality and thus the homogeneity of the coating process. In-vitro dissolution tests reveal more sustained release for the O_3-based process than for the H_2O-based one, thus underlining the benefit of O_3 in providing uniform and conformal coatings. However, little to no difference between TMA/O_3 and TMA/H_2O ALD is observed on lactose particles with amorphous surfaces. In fact, such amorphous surfaces firstly are inherently inhomogenous across the particles and secondly present micropores, as suggested by BET measurements. This inevitably leads to non-conformal films regardless of the co-reactant and moreover results in both surface and subsurface growth.

8:45am **AA3+AF+EM-WeM-4 A High Vacuum Plasma Enhanced Atomic Layer Deposition System for Depositing Very Reactive Metals***, **Feng Niu**,* SVT Associates, Inc.

Most of metal elementals deposited by ALD or PEALD so far are less electropositive or relatively stable. Very reactive metals which are defined as highly electropositive elements(electronegativity c <1.8) including alkaline, alkaline earth, group III, some transition and rare earth metals are needed for applications such as batteries, improved adhesion, barriers, etc.. However they have been proved very difficult to deposit in a conventional thermal ALD or PEALD reactor due to thermodynamic limitation, impurity requirements and unavailability of proper precursors and reducing agents.

A new high vacuum PEALD system achieving base pressure at level of 10^{-8} Torr range with a high efficiency hydrogen plasma source was developed and applied to deposit highly reactive metals. The system has demonstrated deposition of pure Mg metal using commercially available Bis(ethylcyclopentadienyl) magnesium ($Mg(CpEt)_2$).[1] Self-limiting performances of Mg was evaluated(Figure1).Results for film characterizations such as surface morphology by atomic force microscopy (AFM), and film composition especially O impurity by x-ray photon-electronic spectrometer (XPS) (Figure2) will also be presented. A binary sequence surface chemistry is suggested that the hydrogen radicals serve to strip the ligands from the metal precursor according to the general overall reaction scheme: $Mg(CpEt)_2+H_2^*$--Mg+2HCpEt.

This system should also be excellent for deposition of many other very reactive metals such as Sr, Ba, Ti, Nb, Zr, Hf, Li, Na, etc., and for borides, carbides and nitrides where the materials are extremely sensitive to contaminants such as oxygen, moisture, carbon oxides, etc…

[1] US patent # US 9828673 B2.

9:00am **AA3+AF+EM-WeM-5 Plasma Properties of High Pressure ALD***, C Qu,* University of Michigan*; **Pulkit Agarwal**, Y Sakiyama, A LaVoie,* Lam Research Corp.*; M Kushner,* University of Michigan

Plasma enhanced atomic layer deposition (ALD) of high quality dielectric films ultimately depends on controlling the fluxes of plasma produced reactive species onto the substrate and into features. In a typical plasma enhanced ALD cycle of SiO_2, the Si-containing precursor is usually deposited in a non-plasma environment. The oxidation step is then conducted by an oxygen containing plasma such as Ar/O_2. In order to produce high fluxes of the oxidizing radicals, which requires high power deposition, while having ion energies onto the wafer with below-damaging energies, the capacitively coupled plasmas are typically operated at pressures of many Torr. Theses pressures with high power produce high radical fluxes, while the collisional nature of the sheath results in low ion energies. There are several challenges in optimizing this system, including uniformity of reactant fluxes, controlling ion energies and minimizing damaging UV/VUV fluxes.

Results from a computational investigation of high pressure capacitively coupled plasmas designed for plasma enhanced ALD of SiO_2 will be discussed, with the goal of providing insights to the tradeoffs to simultaneously optimizing deposition conditions. Consequences of varying fluxes on uniformity of deposition in moderate aspect ratio features will also be discussed. The modeling platforms used in this study are the Hybrid Plasma Equipment Model (HPEM) and the Monte Carlo Feature Profile Model (MCFPM). The example system uses Ar/O_2 mixtures at pressures of 1-5 Torr, with power deposition of up to a few kW. The fundamental plasma properties of this operating regime (e.g., plasma and radical densities, electron temperature, reactive fluxes to the substrate, sources of ionization), ion energy and angular distributions (IEADs) to the substrate will be discussed. Feature scale modeling will correlate the reactive fluxes to deposition uniformity.

* Work supported by LAM Research Corp. and the DOE Office of Fusion Energy Science.

9:15am **AA3+AF+EM-WeM-6 Remote Plasma Atomic Layer Deposition of Gallium Oxide Thin Films using Trimethylgallium and Oxygen Plasma***, H Hao, Y Shen, J Zhang, **Xiao Chen**,* Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China

Because of its large band gap and many other excellent properties, gallium oxide (Ga_2O_3) is being considered as an important oxide semiconductor for large power transistors, UV optoelectronics and solar cells, etc. Particularly, amorphous Ga_2O_3 is now attracting great interest as gate dielectric and surface passivation layer in transistors. In this work, we have deposited high quality Ga_2O_3 thin films by remote plasma atomic layer deposition (RP-ALD) with trimethylgallium (TMGa) and oxygen plasma. The deposition rate was constant at 0.36Å/cycle within a wide process window from 100 to 400 ℃. X-ray photoelectron spectroscopy (XPS) indicates the presence of gallium, oxygen, and carbon elements with content of ~37.4, ~54.5 and ~8.1 at % respectively in the Ga_2O_3 thin films deposited on silicon substrate at 250℃. The carbon impurity in the film was reduced by ~ 34% comparing with previous reported results[1]. Atomic force microscopy shows smooth surface morphology with a small root-mean-square roughness of 0.156nm. Furthermore, Ga_2O_3 films were successfully deposited on silicon, sapphire and GaN surfaces, indicating the low substrate selectivity that is beneficial to the III-V device fabrication . X-ray diffraction reveals no any crystallization happened in the amorphous Ga_2O_3 films after annealed at a high temperature up to 900℃, under O_2 atmosphere for 90 sec in a rapid thermal annealing system. The excellent thermal stability and high uniformity of Ga_2O_3 thin films deposited by RPALD are very critical to further improve the stability of III-V devices.

Reference:

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9:30am **AA3+AF+EM-WeM-7 Impact of Substrate Biasing during Plasma-enhanced Atomic Layer Deposition on Dielectric Breakdown of Al_2O_3 Thin Film***, **Hyun Soo Han**, M Winterkorn, Y Kim, K Lee, T Yong, K Bae, W Park, P Schindler, F Prinz,* Stanford University

The plasma as reactants in atomic layer deposition process enables a great flexibility in processing conditions and a wide spectrum of material properties. In this study, we demonstrate the tunable electrical property of Al_2O_3 thin film through the substrate biasing during the plasma-enhanced atomic layer deposition. We modulate the substrate bias voltage from 0 to 150 V and evaluate its impact on growth per cycle, mass density and electrical breakdown strength. By applying substrate bias of ~ 20 V during the deposition, an impressive breakdown strength of 0.96 V/nm is achieved, which is approximately 11% higher value than that of the film prepared without substrate bias. Our results demonstrate that the plasma energy control via substrate biasing in the plasma-enhanced atomic layer deposition process is able to be a promising technique in optimizing materials' properties for various electronic or optoelectronic devices.

9:45am **AA3+AF+EM-WeM-8 Growth Mechanism of High-k Y_2O_3 on GaAs(001)-4×6 using *in-situ* Cycle-by-Cycle ALD and Synchrotron Radiation Photoelectron Spectroscopy***, C Cheng,* National Chia-Yi University, Republic of China*; **Wan-Sin Chen**, Y Cheng, L Young, H Wan,* National Taiwan University, Republic of China*; C Yang,* National Tsing Hua University, Republic of China*; K Lin,* National Taiwan University, Republic of China*; T Pi,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

Atomic layer deposited (ALD) high-k dielectrics on semiconductors with thickness from sub-monolayer (ML) to nano-meter (nm) has become a norm in the fabrication of metal-oxide-semiconductor field-effect transistors (MOSFETs).[1,2] The high-performance nano-electronic devices demand scaled-down nm thick oxide layers. Moreover, a low interfacial trap density (D_{it}), the most critical property for the device, depends on the initial oxide growth on semiconductor. Literature contains many studies on ALD oxide films on semiconductors, but few studies have investigated the oxide growth mode in the embryo stage. Thus, the present investigation is motivated to reach the fine region of a single precursor molecule in contact with a single surface atom of a semiconductor substrate. We specifically selected the system of ALD-Y_2O_3 on freshly molecular beam epitaxy (MBE) grown pristine GaAs(001)-4x6. The oxide film is a single-domain single-crystalline cubic phase with a surface normal (110).[3,4] The D_{it} is low of mid 10^{11} $cm^{-2}eV^{-1}$, having a flat D_{it} distribution within the GaAs band gap without a peak bulge in the mid-gap.[5] We have studied the interfacial electronic structure with the film sub-ML to nanometers thick using *in-situ* synchrotron radiation photoelectron spectroscopy (SRPES). In this talk, we will present the growth mechanism of ALD-Y_2O_3 adsorption on GaAs(001)-4×6 with different cycles of deposition in an atomic scale. The pristine p-type MBE-GaAs(001)-4×6 surface was grown in an integrated ultra-high vacuum (UHV) growth/analysis system.[6] After each MBE and ALD deposition, the sample was *in-situ* transferred to National Synchrotron Radiation Research Center (NSRRC) for SRPES measurements with a UHV portable chamber, in which the vacuum is maintained below 5 x 10^{-10} torr. In the embryo stage, we found that $Y(EtCp)_3$ precursors mainly undergo a charge transfer to the faulted As atoms on the GaAs(001)-4x6 surface. Upon H_2O co-reactant deposition, followed N_2 purge, the footed As atoms are readily removed. Moreover, the oxygen atoms in H_2O take over the bonding role with the underneath Ga atoms and lines of Ga-O-Y bonds stabilize the Y_2O_3 film on the GaAs substrate. After one-monolayer Y_2O_3 formed, the coordinatively unsaturated Y-O pairs of Y_2O_3 open the next ALD cycle of alternated $Y(EtCp)_3$ and H_2O process.

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Emerging Materials
Room 104-106 - Session EM1-WeM

Battery and Energy Storage I

Moderators: Seungmin Hyun, Korea Institute of Machinery and Materials, Dongping Lu, Pacific Northwest National Laboratory

8:00am **EM1-WeM-1 Enhanced Thermal Stability of LTO Electrode by Atomic-Layer-Deposited Al_2O_3***, J Yoon, **Seunghoon Nam**,* Korea Institute of Machinery and Materials, Republic of Korea*; K Park, T Yoon,* ISAC Research Inc.*; H Park,* ISAC Research Inc., Republic of Korea*; S Hyun,* Korea Institute of Machinery and Materials, Republic of Korea

Despite of several inherent advantages as high-rate capability and cycling stability of $Li_4Ti_5O_{12}$ (LTO), the gas generation, as a result of the undesired reactions with commercial electrolytes, has been a challenge for the electric-vehicle (EV) application of the material as a negative electrode for Li-ion batteries. Since the gas generation from LTO tends to be accelerated under high temperature (~40 - 60˚C), the thermal stability of LTO should be guaranteed during discharge of the batteries for EVs. In order to mitigate such technical issue, a thin layer of Al_2O_3 (~1 nm) was deposited on the LTO electrode by an atomic layer deposition (ALD), and the resulting electrochemical stability was accessed by cycling cells under 60˚C. The retention of capacity after 500 cycles clearly shows that Al_2O_3-coated LTO outperforms the bare one, with the discharge capacity retained 98% of the initial value. Analysis by TEM with XPS corroborates suppressed surface reaction of the coated LTO, while the uncoated one exhibits the phase transformation of (111) to (222) plane, as indicated by earlier literatures.

8:15am **EM1-WeM-2 Electrochemical Performance of Atomic Layer Deposited Zinc Oxysulfide Thin Film in Li-ion Battery***, Soumyadeep Sinha, J Heo,* Chonnam National University, Republic of Korea

In the recent time, the sustainable and eco-friendly rechargeable energy sources are in high demand to obtain the global environmental pollution free energy storage. Therefore, the choice of Li-ion batteries is not only the power source of the portable electronic gadgets but also for the next-generation electric vehicles. This factor eventually leads to the investigation of new electrode materials to maximize the energy/power density per unit mass as well as per unit area or volume of the active materials. Therefore, the 3D-porous conducting scaffolds coated with active electrode materials or the free-standing electrode materials are the need for the hour. In this regard, zinc (Zn) based materials always have a great importance in any field of energy applications due to its earth abundance, low cost, eco-friendly nature with an easy synthesis process by a variety of deposition techniques. On the other hand, atomic layer deposition (ALD) technique is a great tool for the conformal deposition of a thin film with a precise thickness and desired stoichiometry on any randomly oriented 2D/3D substrates.

In this study, zinc oxysulfide ($ZnO_{1-x}S_x$) thin films on stainless steel (SS) current collector were deposited by ALD which were directly used as an anode material in Li-ion battery without any carbon and binder. The electrochemical performance of the anode material was investigated by cyclic voltammetry (CV) measurements against Li in a half cell configuration which showed prominent redox-peaks during both cathodic and anodic process. A stable discharge capacity of above 500 mAh g^{-1} was obtained at 100th cycle during the charge-discharge cycling performance of this electrode at a high current density of 1 A g^{-1} which was significantly higher than the pristine ZnO and ZnS. Thus, this work can be presented as a typical approach to study the electrochemical responses of a double-anion compound active material which can be easily obtained with a desired stoichiometry with high precision by ALD.

8:30am **EM1-WeM-3 Interfacial and Surface Design of Electrode by ALD and MLD for Next-generation Batteries***, Xueliang (Andy) Sun,* University of Western Ontario, Canada **INVITED**

The interface of electrode-electrolyte in Li batteries is root for poor cell lifetimes mainly due to various side reactions. The use of surface coatings to control of the electrode-electrolyte interface is an important strategy to design new electrodes. Atomic layer deposition (ALD) and molecular layer deposition (MLD) are ideal coating techniques to control the interface and surface of the electrodes in various battery systems [1]. This talk will include three parts:

In the first part, I will report our work on the applications of atomic layer deposition (ALD) in Li ion batteries including synthesis of coating materials such as Al_2O_3, ZrO_2, TiO_2, $AlPO_4$ and $LiTaO_3$ and $LiNbO_3$ as well as the ALD coating materials to modify cathode (NMC) [2].

In the second part, we will discuss MLD alucone coating on Li-S batteries operating at 55C [3].

In the third part, we will discuss our recent results on ALD Al_2O_3 and MLD alucone coatings on Na metal for Na ion batteries and Na-Air batteries [4,5,6].

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9:00am **EM1-WeM-5 Biodegradable ALD Materials for the Packaging of Thin Film Batteries for Implantable Medical Devices***, Messaoud Bedjaoui, S Poulet,* Univ. Grenoble Alpes, CEA, LETI,, France

Nowadays, biodegradable electronics are highly expected to play an important role to achieve a variety of medical applications and more particularly for transient medical devices. In fact, the implantable biodegradable electronic devices provide shorter-term therapeutic function for predetermined periods without any recourse to secondary surgical removal. In the meantime, the power supply of biodegradable electronics must be adapted by providing compatible energy sources. Thin Film Batteries (TFB) offer a unique combination of energy densities and safety properties that are attractive as an energy-storage. In practice, the ideal solid TFB should be biocompatible, and comprise biodegradable materials that would satisfy device power requirements and benignly degrade thereafter.

The purpose of this work is to evaluate the potential biodegradable materials obtained by ALD (Atomic Layer Deposition)/MLD (Molecular Layer Deposition) techniques for the packaging of TFB. The packaging materials can gradually degrade in an in vivo environment within an expected timeframe, during which the TFB is protected before fully dissolving. A judicious design of the packaging strategies can ensure an equilibrium between TFB lifetime and bioapbsorption timelines that therefore conditioning the TFB effectiveness.

First, we explore the biodegradability properties of Al_2O_3, TiO_2 and alucone materials obtained as single layers as well as multilayers at low temperature range (80°C-150°C). In vitro degradation tests employ the exposition to Phosphate Buffer Saline (PBS) and Hank’s Balanced Salt Solution (HBSS) for several weeks at different temperatures (37°C-67°C). In order to establish the biodegradation kinetics, the different structures have been characterized using infrared spectroscopy, scanning electron microscopy (SEM) and complementary analysis (spectroscopic ellipsometry, X-ray photoelectron spectroscopy) before and after exposition to PBS and HBSS saline solutions. The first results seem to prove the biodegradability characteristic of the selected materials. However, the degradation kinetic (from few hours to 4 weeks) may perform very differently depending on the exposition conditions (temperature, PBS, HBSS). It is quite clear for alumina layers in comparison to other materials (Figure 1 and Figure 2). On the other way, we demonstrate in this work that the introduction of multilayer structures (Al_2O_3-Alucone; Al_2O_3-TiO_2) permits the monitoring of this degradation. Finally, the developed structures transferred on TFB devices shown that the electrochemical performances is prolonged by using ALD/MLD materials but it instantaneously damaged without packaging.

9:15am **EM1-WeM-6 Enhanced Conductivity in Thin-Film Solid-Composite Electrolytes for Lithium-Ion Batteries by Combining Molecular and Atomic Layer Deposition***, Simon Hollevoet, K Gandrud,* IMEC, Belgium*; A Patil,* KU Leuven, Belgium*; B Put, P Vereecken,* IMEC, Belgium

Improvements in energy storage are a critical aspect to enable future applications, such as the Internet of Things (IoT), which will lead to an exponential growth in wireless sensors and autonomous microsystems. Currently, planar solid-state thin-film lithium and Li-ion batteries are commercially available but have limited capacity (<0.3mAh/cm2). To meet the future demands in microelectronics in terms of safety, power and energy density the need for all-solid-state 3D thin-film Li-ion batteries arises [1], i.e. there is a need for batteries consisting of thin-films deposited conformally on high aspect ratio substrates.

Here, we present thin-film solid-state composite electrolytes (SCEs), manufactured by combining molecular layer deposition (MLD) with atomic layer deposition (ALD). The SCEs consist of a nanoporous oxide that provides both mechanical stability and a high internal surface area. This nanoporous oxide is coated with a nanometer thin Li-compound layer to exploit the enhanced ion transport at the interface between oxides and lithium salts, as first reported by Liang [2].

In this work, the SCE showed an enhancement in ionic conductivity of up to a few orders of magnitude compared to the pure Li-compound. Moreover, different enhancements were obtained based on different Li-compound/alumina matrix combinations. The nanoporous alumina matrices were obtained through several post-treatments of alucone deposited by MLD. Subsequently the alumina matrix was coated with lithium-compounds (e.g. Li_2CO_3) by ALD. Thus, this is a novel approach to open up new paths regarding design and development of thin-film solid-state electrolytes. Moreover, the SCEs can be deposited on high aspect ratio features, required for e.g. 3D thin-film batteries, and on conventional particle-based electrodes as protective coating.

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9:30am **EM1-WeM-7 Resolving the Mutual Contradiction between Porosity and Toughness of Carbon Textile for Flexible Supercapacitors*, Do Van Lam*,** *J Kim, S Lee,* Korea Institute of Machinery and Materials

Activated carbons, which are highly porous materials prepared from carbonization of carbon-rich precursors with chemical reagents, have numerous advantages in the current energy storage technologies, but could realize further gains in flexible electronics if their mechanical properties were highly improved. However, so far, the mutual contradiction between porosity and toughness in activated carbons still remains unsolved. By coating a nanothin film via atomic layer deposition on cotton prior to the conventional chemical activation, we prepared a flexibly activated carbon textile with high specific surface area (1065 m^2/g) and greatly enhanced toughness of over 40 folds, thus can be directly used for fabricating high-performance flexible supercapacitors. Our results open a general strategy for resolving the contradiction between porosity and toughness in carbon materials and thus hold great promise towards flexible/wearable electronics.

Emerging Materials
Room 104-106 - Session EM2-WeM
Battery and Energy Storage II

Moderators: Parag Banerjee, Washington University, St. Louis, Neil P. Dasgupta, University of Michigan

10:45am **EM2-WeM-12 Atomically-Precise Interfacial Engineering of Energy Conversion and Storage Materials by ALD*, Neil P. Dasgupta,*** University of Michigan **INVITED**

There has been a dramatic increase in research of nanoscale materials for energy conversion and storage devices due to several advantageous features such as high surface areas, short transport distances, and tunable material properties. However, with these benefits come challenges. In particular, the ability to precisely control the properties of surfaces and heterogeneous interfaces limits the performance of many of these devices, and requires novel approaches. Additionally, the ability to manufacture materials with precise control of heterogeneous features in three dimensions and at length scales spanning from atoms to meters is challenging, requiring complementary processing techniques. To bridge this gap requires novel approaches to design material systems across these length scales, allowing us to fabricate hierarchical structures with deterministic control of geometric and chemical properties.

To address this challenge, the Dasgupta Research Group at University of Michigan focuses on the atomically-precise modification of surfacesandinterfaces to control material assembly and transport phenomena across physical and chemical boundaries. Examples include surface passivation against undesirable reactions at electrode-electrolyte interfaces in batteries, integration of co-catalysts on semiconductor surfaces for solar-to-fuel conversion, and charge transport layers in photovoltaics. The key enabling technology that is used for surface modification is Atomic Layer Deposition (ALD). This atomic-scale modification of surfaces allows for precise control of interactions at heterogeneous interfaces, which can be used to direct self-assembly processes, provide tunability of the optical, electronic, thermal, and mass transport properties of integrated material systems, and encapsulate structures to promote their stability in a wide range of environments. In this talk, I will demonstrate examples of the ALD process for modification of electrode-electrolyte interfaces with an emphasis on "beyond Li-ion" batteries and solar-to-fuel conversion, and provide a perspective on how this versatile approach can lead to the design and manufacturing of hierarchical material systems with "designer" interfaces and interphases.

11:15am **EM2-WeM-14 Minimizing Polysulfide Shuttle Effect in Lithium-Ion Sulfur Batteries by Anode Surface Passivation via Atomic Layer Deposition*, Jian Liu,*** The University of British Columbia, Canada*; D Lu, J Zheng, P Yang,* Pacific Northwest National Laboratory*; B Wang, X Sun,* University of Western Ontario, Canada*; Y Shao, C Wang, J Zhang, J Liu,* Pacific Northwest National Laboratory

Lithium-sulfur (Li-S) batteries have grained increasing attentions as competitive power supply system for electric vehicles, due to their high energy density and low cost of sulfur [1,2]. During the past few years, encouraging progresses have been made to develop novel cathode structure to address the polysulfide shuttle effect and poor conductivity of sulfur. However, the problems associated with Li metal, such as Li dendrite and polysulfide corrosion, remain unresolved. To circumvent the problem, one promising route is to pair a non-Li anode with the sulfur cathode to develop Li-ion sulfur batteries [3,4]. Nevertheless, polysulfide shuttle reactions still occur when using non-Li anodes, leading to limited cycling life and low CE in Li-ion sulfur batteries.

In this work, we developed a surface passivation strategy to minimize polysulfide shuttle effect on those alternative anodes, in order to enable high-performance practical Li-ion sulfur batteries. We used an ultra-thin electron-insulating layer (Al_2O_3), deposited by atomic layer deposition (ALD), to passivate the surface of the non-Li anodes (graphite as an example), with the aim of blocking the electron transfer pathway and alleviating polysulfide shuttle (Figure 1). We found that with the optimal thickness of 2 nm Al_2O_3 coated on graphite anode, the Coulombic efficiency of the sulfur cathode was improved from 84% to 96% in the first cycle, and from 94% to 97% in the subsequent cycles (Figure 2). As a result, the discharge capacity of the sulfur cathode was increased to 550 mAh g^{-1} in the 100th cycle, as compared with 440 mAh g^{-1} when the pristine graphite anode was used. Mechanism study disclosed that the Al_2O_3 passivation layer minimized the formation of insoluble polysulfide (Li_2S_2, Li_2S) on the surface of graphite anode and improved the efficiency and capacity retention of the graphite-sulfur batteries. It is expected that this surface passivation strategy could be also applied to other sulfur based battery systems (with Li, Si, and Sn anodes), to reduce side reactions and enable high-performance sulfur batteries.

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11:30am **EM2-WeM-15 A Facial Way to Prepare Large Areal 3D Porous Carbon via Molecular Layer Deposition and its Application for Lithium Sulfur Batteries*, Yan-Qiang Cao,*** *W Zhang, A Li,* Nanjing University, China

Nowadays, rechargeable batteries with a high energy density and long life are needed in many applications, ranging from portable electronic devices to electric vehicles. Unfortunately, the state-of-the-art lithium ion batteries (LIBs) cannot satisfy these requirements now. Therefore, tremendous efforts are being dedicated toward developing "beyond-lithium-ion" batteries. Lithium sulfur (Li-S) batteries are one of the most promising next-generation energy storage systems with a high capacity of 1675 mAh/g and energy density of 2600 Wh/kg. However, significant issue must be overcome before Li-S batteries can be implemented, such as the highly insulating nature of sulfur and the high solubility/diffusivity of lithium polysulfides in the electrolyte. A great deal of scientific and technological innovations have been proposed to solve these problems, such as optimizing the electrolyte and fabricating composite electrodes of sulfur/polymer, sulfur/metal organic framework (MOF) or sulfur/carbon.

In this work, a novel and facial approach was proposed to synthesis the large areal three-dimensional (3-D) porous carbon. Inorganic-organic hybrid film via molecular layer deposition (MLD) was used as carbon precursor, while metal foam or metal oxide fiber was utilized as sacrifice template. Inorganic-organic hybrid films would be transformed into carbon/oxide by pyrolysis in inert atmosphere. After etching the oxide in carbon and template, 3D porous carbon of various shapes can be achieved. We can gain a large porous carbon of 10*10 cm at present. In addition, as-prepared porous carbon exhibits well flexibility.

Further, a composite cathode system for Li-S batteries was synthesized by loading sulfur onto 3D network of porous carbon via a sulfur melt infiltration method. The 3D porous carbon can offer excellent electrical conductivity, and an appropriate hierarchical pore structure containing the electro-active sulfur facilitates rapid electron/ion transport. More importantly, this cathode system does not require any additional binding agents or conductive additive. A Li-S battery with the sulfur-3D porous carbon cathode shows good electrochemical stability and high rate discharge capacity retention, which delivers a reversible capacity of about 930 mAh/g at the current density of 100 mA/g. Our results indicate the great potentials of MLD derived 3D porous carbon for high-performance batteries.

11:45am **EM2-WeM-16 Enhanced Metal-support Interaction of Ceria Supported Platinum Single Atoms and Subnanoclusters for Room Temperature CO Oxidation***, **Xiao Liu**, Y Tang, B Shan, R Chen,* Huazhong University of Science and Technology, China

The CO poisoning effect is one of the critical problems plaguing platinum (Pt) catalyst, which can limit its activity by blockage of surface active sites and subsequent reaction steps under low temperatures.[1] Such phenomena is quite general considering that CO will be used as reactants or generated as reaction intermediates in many catalytic processes such as CO oxidation, water-gas shift reactions, and fuel cells.[2-3] In view of the high dispersion (smaller Pt nanoparticles) required for catalyst applications, CO poisoning will be only more pronounced, wherein large fraction of coordinately unsaturated edge and vertex sites over-bind CO molecules.[4] Here, we report a method to tackle the CO poisoning effect on high dispersed Pt clusters by enhancing the metal-support interaction. The Pt single atoms and subnanoclusters have been prepared on ceria (CeO_2) nanorods by optimizing the atomic layer deposition recipe and post-treatment annealing process. The copper doping at the interface of Pt/CeO_2 has been performed to enhance the low temperature CO oxidation activity. The as-prepared copper-doped CeO_2 supported Pt subnanoclusters show excellent CO oxidation activity, which is significantly better than that of the reported subnanocluster and single atom catalysts in previous studies. The results of X-ray photoelectron spectroscopy, *in-situ* CO diffuse reflectance infrared absorption spectroscopy and density functional theory calculations show that the enhanced catalytic activity is due to the activation of lattice oxygen and the decrease of CO binding strength.

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Emerging Materials
Room 107-109 - Session EM-WeA
MLD & Emerging Materials

Moderators: Jiyoung Kim, University of Texas at Dallas, Charles Dezelah, EMD Performance Materials

1:30pm **EM-WeA-1 Physical, Chemical, and Electrical Properties of Molecular Layer Deposited Alucone Thin Films using Trimethyl-aluminum and Hydroquinone*, Seung-Hwan Lee*,** *G Beak, J Lee, J Park,* Hanyang University, Republic of Korea

Molecular layer deposition has been rapidly emerged to fabricate an organic film, showing a self-limited reaction and half-reaction cycle by using metal precursor and/or organic monomer. The deposited films exhibit excellent conformality, uniformity and exact thickness control like atomic layer deposition. Many researcher groups reported alucone films using various organic monomers (ethylene glycol (EG), diethylene glycol (DEG), hydroquinone (HQ) etc.) but they have researched basic process conditions and film properties. [1-2] However, mostly the organic layers are very sensitive to air ambient. The water and oxygen may react with organic frames in MLD layers and destruct/decompose the structure of organic films. So, it is one of big challenges to utilize the functional films in emerging application areas.

In this work, we investigated the physical, chemical, and electrical properties of Alucone films, deposited by trimethyl aluminum (TMA) and HQ. The pristine alucone film didn't show any D and G peak in Raman spectra, indicating a carbon domain evidence. But the annealed alucone film did carbon domains like amorphous graphite carbon layers. The pristine films, including carbon-oxygen and carbon-hydrogen bond, dramatically turned to the dehydrated alucon filme during the annealing process. This change may stabilize the organic structure and improve the air-stability. Spectroscopic ellipsometer (SE), Auger electron spectroscopy (AES), Raman spectra and X-ray photoelectron spectroscopy (XPS) were used to understand film properties. Also, hall measurement and seebeck coefficient measurement were used to measure electrical properties of the annealed alucone film, which showed p-type carrier and conductivity. Thus, the process and material will be a promising layer because the stable organic layer may provide not only new functional surface but also functional coted films in emerging electronic applications.

[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

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1:45pm **EM-WeA-2 Molecular Layer Deposition of Boron Carbide Thin Films*, Suhaib Malik*,** *R Thapa, L Dorsett, S Wagner, A Caruso,* University of Missouri-Kansas City*; D Merrill, J Bielefeld, S King,* Intel Corp.*; M Paquette,* University of Missouri-Kansas City

The drive towards smaller and more powerful integrated circuits (IC) has put increasing strain on both traditional circuit materials and electronics manufacturing. New materials must perform as better electrical components than their predecessors and, as is increasingly becoming the case, meet higher standards of thermal and mechanical properties for performance and miniaturization. The state of the art approach to building IC components is top-down; a pre-built material of a given thickness is etched into. The advent of atomic layer deposition (ALD) extends a top-down approach by allowing for smarter-designed materials with more exact layering and patterning, while also enabling a bottom-up approach by opening the door to capabilities like selective deposition. Boron carbide (BC) films provide a unique solution to the first half of the above problem: they display promising electrical and physical properties for applications ranging from corrosion protection to low-k dielectrics to electrical surface modification to neutron detection. We propose that if BC can be deposited using an ALD growth scheme, it could address many present challenges in engineering micro- and nano-scale electronics and introduce a unique set of materials to the ALD family for other applications. In this presentation we will describe the use of carboranes as molecular layer deposition precursors in growing thin BC films and the effect of growth parameters on deposition behavior.

2:00pm **EM-WeA-3 Achieving Room Temperature and Below Phase Transitions in ALD Doped VO_2 Films*, Virginia Wheeler*,** U.S. Naval Research Laboratory*; A Kozen,* The American Society for Engineering Education*; M Currie, B Downey, D Meyer, C Eddy, Jr.,* U.S. Naval Research Laboratory

VO_2 undergoes a first order crystalline phase transition at a critical temperature (T_c = 68°C), resulting in significant changes in intrinsic electrical and optical properties, especially in the infrared. Optical changes with this phase transition are of particular interest as passive and active components of optoelectronic devices, specifically for thermal regulation. Realizing this type of device often requires the integration of thin, conformal VO_2 films with complex, non-planar structures (like metamaterials). Thus, atomic layer deposition (ALD) is the ideal deposition method in these cases. While the T_c of VO_2 may be appropriate for some applications, others require this transition to occur at lower temperatures. Traditionally, lowering the T_c has been accomplished through inducing strain or doping VO_2 films with small amounts (1-5 at%) of transition metals. Yet, similar doping induced changes have not been shown in ALD VO_2 films. Here, we achieve a T_c less than room temperature through ALD Nb doped VO_2 films.

Previous studies have shown that T_c near room temperature can be obtained through W doping. Unfortunately, the growth window for $W(CO)_6$ and ozone was above 200°C, which is higher than the vanadium precursor (TEMAV) decomposition temperature, rendering it incompatible with the VO_2 process. A variety of other compatible dopants were explored and Nb had the most potential, allowing the T_c to be reduced with minimal degradation in morphology, structure, and optical transition properties.

ALD Nb-doped VO_2 films were formed using supercycles of Nb_2O_5 (TBTDEA-Nb(V), O_3) and VO_2 (TEMAV, O_3) at 150°C on c-sapphire substrates. By varying the ratio of Nb_2O_5 to VO_2 cycles, doped films with 1-7 at% Nb were achieved. Initial studies suggest that the Nb_2O_5 layer may inhibit the subsequent nucleation of VO_2 layers, resulting in non-linear incorporation of Nb. A reduction in T_c of -11.2°C/Nb at% was attained, which is larger than reports of Nb-doped VO_2 films by other growth methods. Additionally, up to ~1.6 at% Nb, the magnitude of the optical transition is maintained while shifting the T_c to 36°C. To attain a room temperature T_c requires 3.3 at% Nb, which is accompanied by a reduction in optical transmission modulation to ~10%. Similarly, a 5°C T_c was obtained with 5.1 at% but with only a 5% optical modulation. TEM images show that films with a reduced optical modulation still have inclusion of amorphous grains, even after ex-situ annealing, which increases with increasing Nb doping. The extent of being able to fully crystallize VO_2 films with high Nb contents will be discussed to determine the realization of usable films with T_c near 0°C.

2:15pm **EM-WeA-4 Ozone Based High Temperature Atomic Layer Deposition of SiO_2 Thin Films*, Su Min Hwang*,** *X Meng, A Lucero, H Kim, S Kim,* The University of Texas at Dallas*; B Hwang,* Dow Chemicals*; J Kim,* The University of Texas at Dallas

Recently, deposition of SiO_2 films with high quality and good conformality has drawn great attention as device structures have become more complicated. Conventionally used LPCVD and PECVD for SiO_2 deposition have limitations in terms of conformal deposition and thickness scalability. Since ALD is expected to overcome the challenging issues, several research groups have reported SiO_2 ALD using $SiCl_4$, SiH_2Cl_2, and Si_2Cl_6 at low temperature (250 – 500°C)). Unfortunately, the ALD films show less dense film qualities compared to thermal oxide [1-3]. For high quality SiO_2 films with good conformality, an ALD process at high temperature is desirable. However, research on high temperature ALD processes is scarce due to the difficulty of the process caused by decomposition of precursor resulting in CVD-like growth instead of self-limiting ALD growth.

In this work, oxidation of silicon wafers using various oxidants (H_2O, O_2 and O_3) was performed using a rapid thermal ALD system to identify if O_3 has higher reactivity for high temperature ALD of SiO_2. Although O_3 has a short lifetime above 300°C due to thermal decomposition, thermal oxide grown with O_3 at 300 to 800°C shows higher thickness compared to oxide films grown using H_2O and O_2. The activation energy of O_3 based process was calculated to 0.07 eV, which is a lower value than those of H_2O based process (0.14 eV) and O_2 process (0.16 eV). Among the possible oxidants, we confirmed that O_3 has a higher reactivity for ALD of SiO_2 due to reactive O radicals. Based on these results, ALD of SiO_2 thin films using Si_2Cl_6 and O_3 was performed at from 500 to 700°C. At 650°C we observe a saturated growth rate of 0.24 Å/cycle at a Si_2Cl_6 exposure of 2.0 10^6 L with fixed O_3 exposure. Growth rate is linear with the number of cycles indicating there is only a small or no incubation period observed. Our findings highlighted that reactivity of O_3 can be maintained at high temperature and it can be applicable to ALD of SiO_2 process.

We acknowledge TMEIC for ozone generator.

2:30pm **EM-WeA-5 Atomic Layer Deposition of High-T_c Magnesium Diboride (MgB_2) Film for Superconducting Radio-Frequency Particle Beam Accelerators***, **Alireza Nassiri**, D Mandia, A Yanguas-Gil, A Mane, J Elam,* Argonne National Laboratory

Atomic Layer Deposition (ALD) as a self-limiting coating process is an ideal technique relatively thick, high quality coating of high-T_c superconductor Magnesium Diboride (MgB_2) on radio frequency copper resonant structures (cavities) for particle beams accelerators. MgB_2 is considered one of the viable materials to substitute bulk niobium for superconducting radio frequency cavities. Utilizing a MgB_2 coating on the inner wall of a copper cavity will allow operation at higher temperatures (20–25 K) than Nb cavities due to the high transition temperature of MgB_2 (39 K) and the high thermal conductivity of Cu. Achieving higher accelerating fields and eliminating expensive capital and operating costs of large liquid helium refrigeration system by using highly efficient and cost effective cryo-coolers are amongst the major benefits of using magnesium diboride. Here, we will present initial results on this ongoing effort.

2:45pm **EM-WeA-6 Commerical Production of ALD-Coated Powders and Polymers***, **Daniel Higgs**,* ALD NanoSolutions, Inc.

Atomic and molecular layer deposition (ALD) can be economically scaled to coat tons of powder, kilometers of polymers and many thousands of specialty objects a day. ALD reached commercial scale for coating various chemistries onto silicon wafers in the semiconductor industry in the 1990s, which today is a multi-billion dollar market. ALD is now becoming the method of choice for coating ultrathin, precisely controlled films onto particles and other new material substrates.

This talk will discuss the cost-effective commercial production of ALD-enabled materials at >1000T/yr of powders and >50M m2 /yr of polymers. We will cover batch and continuous ALD systems that enable this high volume production as well as discuss various markets for the materials processed in these systems. Two current commercial products will be touched on and other pre-commercial products will be discussed.

ALD Nano helps customers solve particle material challenges by perfecting the necessary ALD coating chemistries, process conditions and manufacturing equipment systems. Our global leadership position is ALD on powders, also known as particles or particle ALD. Many Fortune 500 companies are among our customers and supply channel partners. ALD on particles has many benefits including:

- Superior precision and cost-effectiveness compared with chemical vapor deposition (CVD) and other techniques enable new or better applications for known substrates with improved end-device performance, lifetime, cost and safety.
- Novel atomic-scale material designs can be created with significant value to materials supply chain customers and end-device partners.
- Substrate functionality improvements occur by changing physical characteristics of particles including enhanced (or reduced) chemical stability, flowability, corrosion, oxidation, conductivity, hydrophobicity, optical properties, material compatibility, dispersion, sintering control, barrier performance, and other improvements that result in better end device performance.
- Particle agglomeration does not happen with proper ALD process conditions, regardless of particle size, shape and morphology.

3:00pm **EM-WeA-7 Ruthenium: Advanced Nodes and Supply Chain Implications***, **Oliver Briel**, D Zeng, A Wilk,* Umicore AG & Co. KG, Germany

Advanced new materials and chemistries may play an important role to extend Moore's law to continue miniaturization of chip design while at the same time increasing their performance. One of these promising materials is ruthenium partly due to its unique properties of interest to the industry.

In the early 2000's, there was a Ru hype at the R&D scale, however little or none of the new materials made to HVM, because the industry solved the problems by extending existing technologies, or by introducing alternative materials. Today we are in a similar situation as then except it seems to be more difficult to extend lifetime of the existing technologies or find other alternatives, hence we sense the optimism in ruthenium adoption for advanced chip nodes as foreseen in technology roadmaps provided by leading research organizations supporting the industry. While the outcome of Ru adoption remains to be seen, one thing we have learned is that many industry participants shared reservation in ruthenium based application development, because of the notion this material system being very "expensive" with "unpredictable price movements" and "unstable supply".

Umicore is a traditional platinum group metals company, active in the field for many decades, if not centuries. Through this presentation and discussion, we hope to shed light on and demystify the black box of PGM market dynamics. We will discuss a number of topics, such as where do PGMs come from, how much are available, which technologies/applications are the drivers of their demands, how are the PGMs priced, what procurement strategies can be used to mitigate cost impact due to price fluctuations, how does metal reclaim work, and who are among the key players in the value chain, all with a special focus on ruthenium.

In addition, we will introduce our most recent advanced Ru metal precursors as potential candidates for ALD and MOCVD applications.

3:15pm **EM-WeA-8 An Alternative Precursor for Safe Deposition of Aluminum Oxide Thin Films***, **Liao Cao**,* Ghent University, Belgium*; F Minaye Hashemi,* Delft University of Technology, Netherlands*; F Mattelaer,* Ghent University, Belgium*; J van Ommen,* Delft University of Technology, Netherlands*; C Detavernier,* Ghent University, Belgium

Aluminum oxide is widely used as a barrier layer, dielectric film and encapsulation material due to its excellent chemical and thermal stability, high field strength and high resistivity. Controlled deposition of aluminum oxide thin films via atomic layer deposition (ALD) is a well-developed process with applications ranging from semiconductor electronics to large-scale coatings.The most commonly used precursor for deposition of Al_2O_3 via a thermal ALD process is trimethylaluminum (TMA). TMA has a high vapor pressure and is very reactive towards most surfaces, acting as an ideal precursor for deposition of Al_2O_3 at various temperatures. However, TMA is pyrophoric, toxic, corrosive and expensive when aiming to coat surfaces at large scale, such as coating powders or roll-to-roll processes. Thus, alternative low-cost and safe precursors for deposition of alumina would facilitate economical and environmentally sustainable manufacturing of new surfaces and materials.

In this work we investigate an alkoxide precursor as a safe and stable alternative to TMA. Aluminum tri-isopropoxide (TIPA) is studied as the Al source for ALD of Al_2O_3 when different oxidizing agents including water, plasma and ozone are employed in the deposition process. We have explored the deposition of Al_2O_3 using TIPA in ALD systems operating in vacuum and atmospheric pressure conditions. Deposition process has been studied on both planar substrates and on different nanoparticles to explore the feasibility of using TIPA for various purposes including large-scale applications.

During thermal and plasma processes in vacuum ALD, we show a growth window of Al_2O_3 from 140°C up to 300°C . Growth rates achieved in the plasma process are comparable to the thermal ALD of TMA and water (1.1Å/cycle). X-ray reflectivity analysis confirm an increasing density of Al_2O_3 film when deposition temperature is increased. Scanning electron microscopy and atomic force microscopy show deposition of smooth films when TIPA is used as a precursor. X-ray photoelectron spectroscopy studies confirm stoichiometric deposition of Al_2O_3 with no presence of carbon contamination. The thermal water process at atmospheric pressure ALD (AP-ALD) resulted in a growth rate up to 1.1 Å/cycle with no residual carbon. No growth was observed when ozone was used as the oxidizing agent under atmospheric pressure conditions. AP-ALD on nanoparticles shows different growth modes on TiO_2 versus SiO_2 nanoparticle surfaces confirmed by transmission electron microscopy analysis. Using TIPA as an ALD precursor would open up the possibility for a safer and cost-effective process for deposition of Al_2O_3 in various applications.

4:00pm **EM-WeA-11 Application of PEALD Technique to the Fabrication of Vertical TFT for the Ultra High-Resolution Display***, **Kwang-Heum Lee**, S Lee, H Yeom, J Ko,* Korea Advanced Institute of Science and Technology, Republic of Korea*; C Hwang,* Electronics and Telecommunications Research Institute*; S Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

1. Introduction

In nowadays, VR (Virtual Reality) and AR (Augmented Reality) are thought to be the key applications of future display. However, there still remain several obstacles, and one of them is the low resolution of display. To solve this problem, higher pixel density of several thousand PPIs is strongly required. Oxide semiconductor vertical thin-film transistor (VTFT) can be an appropriate candidate for the backplane component of the ultra high-resolution display. Its vertical channel structure makes it possible to reduce footprint size, which helps to make the pixels to be smaller and brighter at the same time. And also, it is possible to fabricate sub-micron scale channel length TFT by using the conventional photolithography techniques for the display industry more easier. This can give us high on-current characteristics. With these reasons, we conducted research for the oxide semiconductor based VTFT and tried to improve its electrical properties.

2. Experiments

Oxide semiconductor based VTFTs were fabricated on thermally oxidized Si wafer substrates. We used ITO for the source/drain electrodes, SiO_2 for the spacer, InO_x via plasma-enhanced atomic layer deposition (PEALD) method for the active layer, and Al_2O_3 for the protective layer (PL) + gate insulator. PL layer was adopted to reduce gate leakage current. All patterning steps except for the active and PL layer were conducted by dry-etching. Although, VTFTs have vertical spacer with taper angle of ≈80°, it does not make any problems with step coverage due to adopting PEALD technique for deposition of active & gate insulator layers.

3. Results

From our experiments, we could fabricate the VTFT with high on-current driven at low voltage. In addition, through pre-annealing process of InO_x active layer under oxygen atmosphere, we could verify broader process window for the post-annealing, which is needed for the LCD display. These results indicates the possibilities of VTFT for the Ultra High-Resolution display.

4. Conclusions

In this paper, we investigated the possibility of fabricating oxide semiconductor VTFT using PEALD. Through this result, we will continue to conduct our experiments for the process optimization and adopting to the ultra high-resolution display panel.

4:15pm **EM-WeA-12 Effect of Substrate on MoS_2 Deposited by Plasma-enhanced Atomic Layer Deposition***, **Asad Mughal**, T Walter, K Cooley,* The Pennsylvania State University*; A Bertuch,* Veeco-CNT*; S Mohney,* The Pennsylvania State University

Due to their promising physical properties, semiconducting two-dimensional transition metal dichalcogenides (2D TMDs) are a materials class receiving intense research attention. Molybdenum disulfide is one of the most widely studied materials in this class and has the potential for applications ranging from electronics to catalysis. However, achieving large-area uniform growth of MoS_2 is challenging and is typically accomplished at elevated temperatures using chemical vapor transport, chemical vapor deposition, or related techniques. Plasma-enhanced atomic layer deposition (PEALD) is a promising method for achieving control of film thickness at the atomic scale and with growth temperatures low enough to accommodate integration into traditional semiconductor device fabrication processes. In this work, we use PEALD to grow thin layers of MoS_2. Using the co-reactants $(N^tBu)_2(Nme_2)_2Mo$ and H_2S:Ar plasma, depositions were carried out in a hot-walled PEALD system from 250–450 °C. Higher purity layers were achieved using a sapphire rather than silica plasma tube. Films were characterized by spectroscopic ellipsometry, XPS, TEM, AFM, and resonance Raman spectroscopy (RRS) to determine growth rate, morphology, purity, and crystalline quality. RSS revealed the number of layers of MoS_2 ($A_{1g}(\Gamma)$- $E_{2g}(\Gamma)$) as well as crystalline quality ($A_{1g}(\Gamma)/LA(M)$). Interesting variations were observed among films deposited on different substrates, with better crystalline quality on (0001) sapphire than on SiO_2/Si or (0001) GaN/sapphire. Molybdenum disulfide was controllably grown down to single-layer thicknesses by adjusting the number of growth cycles. When deposited on silicon nitride membranes, MoS_2 layers were found to be polycrystalline with the (0001) plane parallel to the substrate. However, substrate-dependent out-of-plane growth was observed for thicker films, especially on silicon nitride, SiO_2/Si, and sapphire. Higher growth temperatures, as well as post-deposition annealing under sulfur vapor, was shown to increase the crystallinity of the films. We anticipate that this PEALD growth technique will be suitable for a wide array 2D TMDs thin films and devices.

4:30pm **EM-WeA-13 Single-crystal Ternary Perovskite $YAlO_3$ Epitaxial Growth on GaAs and GaN via Y_2O_3 Template Overcoming a Large Film/Substrate Lattice Mismatch***, **L. Bo-Yu Young**, C Cheng, K Lin, Y Lin, H Wan,* National Taiwan University, Republic of China*; R Cai, S Lo,* Industrial Technology Research Institute, Republic of China*; M Li,* National Applied Research Laboratories, Republic of China*; C Hsu,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

It is a challenge to perfect a hetero-epitaxial growth. Earlier successful examples are rare-earth metals/Nb/sapphire,[1] which led to the discovery of anti-ferromagnetic coupling through non-magnetic media, based on which the giant magnetoresistance (GMR) for the high-density recording was established, and GaN/sapphire, which led to the blue light emitting diode and lasers. Integrating atomic layer deposited (ALD) single-crystal perovskite onto semiconductor combines rich properties of the perovskites with advanced electronic and opto-electronic devices. Previously we presented hexagonal perovskite $YAlO_3$ (H-YAP) on GaAs and GaN. We have achieved excellent single crystal H-YAP on GaAs(111)A using ALD sub-nano-laminated Y_2O_3/Al_2O_3 multi-layers through post-deposition rapid thermal annealing with temperatures above 900^{o}C.[2,3]

From the high-resolution scanning transmission electron microscopy (STEM) images, we have observed a single atomic layer of Y-O at the YAP/GaAs(001) and /(111)A interfaces. In this work, we have further investigated the initial growth of the H-YAP on GaAs(111)A and GaN with and without a Y_2O_3(111) single crystal template. Fig. 1 shows the X-ray diffraction results of H-YAP grown on the Y_2O_3 template after 900^{o}C anneal. The pronounced fringes shown in Fig. 1(a) indicate excellent crystallinity of H-YAP and sharp interface between H-YAP and Y_2O_3. The narrow FWHM ~0.019^{o} of H-YAP(0004) θ-rocking scan confirmed the excellent crystallinity. From the STEM image shown in Fig. 2, H-YAP grew directly from Y_2O_3. The Y-sub-lattice in the atomic packing of Y_2O_3(111) has a hexagonal-like structure with a 2-D lattice constant a= 3.75 Å, similar to that of H-YAP(0001) with a = 3.68 Å as shown in Fig. 3. The top Y (Y-O) layer in the Y_2O_3(111) is the initial Y (Y-O) layer of the H-YAP. Notice their structural similarity. The excellent crystallinity of H-YAP may be attributed from the excellent starting Y_2O_3 layer with a FWHM ~0.017^{o} of Y_2O_3(444) θ-rocking scan. For the H-YAP/GaAs(111)A, the FWHM of H-YAP(0004) θ-rocking scan is ~0.026^{o} despite a large lattice mismatch ~8.5%. Fig. 4 shows the STEM image of the H-YAP grown on GaAs(111)A, where a Y-O layer was observed between H-YAP and GaAs dumbbell at the interface. This Y-O layer may also be the starting layer of the single crystal H-YAP. Our recent work on the initial growth of ALD- Y_2O_3 on GaAs using in-situ synchrotron radiation photoemission may shed the light on the understanding of the interfacial electronic characteristics, namely the chemical bonding.[4]

LBY, CKC, and KYL have contributed equally to this work.

CHH, JK, and MH are the corresponding authors.

Author Index

Bold page numbers indicate presenter

Author Index