Aerosolization of Inhaled Drug Particles: Towards Printable Electronic Devices

4:00pm AA1-Moa-11 ALD and PE-ALD of High-Mobility Zinc-Tin-Oxide Semiconductor Layers: Towards Printable Electronic Devices, T Cho, C Allemang, N Farjam, O Trejo, S Ravan, R Rodriguez, K Barton, R Peterson, Neil Dosgupta, University of Michigan

Transparent amorphous oxide semiconductors (TAOS) are a valuable class of functional materials that are being explored for applications in flexible electronics. To enable next-generation devices, ranging from personal health monitoring to electronic textiles, there is a need for new material processes that enable low-temperature processing while maintaining high-quality device performance. Furthermore, the use of non-planar substrates requires deposition processes that can produce uniform, reproducible material properties without line-of-sight limitations. Therefore, there has been a push towards printable electronic devices, which can be fabricated on flexible substrates, enabling a wide range of applications from wearable electronics to rollable displays. One of the promising materials for these applications is high-mobility zinc-tin-oxide (ZTO) film, which can be deposited using atomic layer deposition (ALD) and plasma-enhanced ALD (PE-ALD) processes.

In this work, the viscosities of the ALD precursors, such as TMAOx (trimesitylamine/oxo), are improved, leading to lower powder cohesiveness. As suggested by atomic force microscopy, this results in a notable increase in fine particle fraction (FPF: % < 5 μm, i.e., particle size range relevant for inhalation) for the SiO2- and TiO2-coated particles, respectively. The higher FPF after the ALD process is attributed to the lower interparticle force which reduces the powder cohesiveness, as suggested by atomic force microscopy. Finally, the aerosolization properties are retained even after exposure at 40 °C and 75% RH for 1 month, demonstrating a good shelf performance.

Method: The degradation of the ALD-coated Si/SiO2/Al interdigitated electrodes (IDEs) was investigated. The ALD films were deposited with PICOSUN® R-200 Advanced ALD reactor at different temperatures of 85, 125 and 200°C. Metal oxides such as Al2O3, SiO2 and HfO2 and their laminates were deposited in order to screen the temperature and material effect on the barrier properties. For the in-vitro study through accelerated aging tests the samples were wire-bonded and placed on phosphate buffered saline (PBS) solution and kept at 85°C. The film degradation was on-line monitored by resistance measurements every 10 minutes until a notable rise in resistance value indicating failure of the barrier material.

Results: We will present the results from in-vitro accelerated tests and compare those to our previous excellent results with SiO2-HfO2 [1]. Both the studies show that the best ALD-laminates can last without failure in accelerated aging tests in PBS (85/87°C) at least 100 days corresponding over 10 years at human body (37°C). We will also present the ISO 10993-5 standard cytotoxicity test results. The results highly support ALD as a hermetic and biocompatible corrosion resistant layer in future medical devices and implants.

References:
[1]https://doi.org/10.1002/adfm.201806440

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been significant interest in ALD as an approach to engineering high-quality TAOS layers for devices such as thin-film transistors (TFTs).\(^1\)

Among the various TAOS materials, zinc-tin-oxide (ZTO) is being explored as an alternative to indium-gallium-zinc-oxide (IGZO), as it has the potential to reduce manufacturing cost significantly by utilizing earth-abundant elements\(^2\). However, to date, there have been relatively few reports of TFT device performance using ALD ZTO layers, and high-temperature post-deposition anneals have been required to achieve enhancement-mode devices with high field-effect mobility (\(\mu_F\)). To overcome these limitations, in this study, we explore the role of oxidizers, including water and O\(_2\) plasma. We demonstrate that through rational control of the process conditions and combining these oxidizing species in a super-cycle recipe, we can achieve \(\mu_F\) values of > 13 cm\(^2\)/V\(\cdot\)s in films as-deposited at 200°C. Even higher mobility values can be achieved when post-deposition anneals are performed. The process-structure-property relationships of these high-mobility ZTO films will be described, including the role of zinc:tin ratio, deposition temperature, and post-deposition treatments.

To demonstrate a pathway towards bottom-up, printable devices, area-selective ALD of ZTO is demonstrated using printed polymer inhibition layers. By using electrohydrodynamic-jet (e-jet) printing\(^3\), we demonstrate the ability to pattern devices with \(<1\) \(\mu\)m resolution, well below the resolution of traditional inkjet printing. Finally, printed TFTs were fabricated, demonstrating well-behaved device performance, including an on/off current ratio of almost 10\(^4\). This research presents a pathway towards printable electronic devices based on low-temperature ALD/PE-ALD processing, which is compatible with flexible/stretchable substrates and does not require any clean-room processing.


1:30 PM 


The rapidly spreading Internet-of-Things is accelerating MEMS (Micro-ElectroMechanical Systems) industry’s to deliver highly sensitive and miniaturized self-sensors with low consumption and cost effective production process. Up to now, no consistent study has emerged to propose the optimized configurations for piezotronic materials properties and electrodes interface configurations on sensors for reliable microfabrication processing for MEMS.

By the means of Atomic Layer Deposition (ALD), we developed piezotronic strain sensitive sensors integrated in polyimide cantilevers, where a zinc oxide (ZnO) thin film is deposited on top of patterned interdigitated platinum electrodes (Figure 1). Due to its high film conformity, low temperature processing, self-limiting nature and stoichiometric control at the nanoscale level, ALD technique has emerged as an ideal technique to add new functionalities in MEMS. ALD technique can coat high aspect ratio topographies, with flawless interfaces and low temperature process compatibility on organic flexible surfaces. We propose to rationalize the ALD processing to obtain wurzite polycrystalline zinc oxide thin films with a privileged (002) orientation and to make it compatible with microfabrication processing on polymer. Hence, Schottky junctions are realized by microstructuring interdigitated micro-combs at the interface of the high work function metal and the semiconductor piezoelectric ZnO thin film. This piezotronic junction has the particularity of an exponential dependence of the flowing diode current as a function of the applied mechanical strain. The sensitivity is thus greatly improved with gauge factor higher than 100. Our associated noise analysis and signal to noise ratio measurements estimated minimal strain detection of 10\(^{-6}\).

In the last stage of this work, we will present the strain sensors size miniaturization for integration in microcantilevers in a full polymer body, compatible with AFM (Atomic Force Microscopy) scanning probe operations (Figure 2). The influence of the ALD deposition parameters on the sensors electromechanical transducing properties will be reported as well. Thus, we propose a promising way of zinc oxide thin film processing by ALD for a reliable microfabrication processing to obtain ultrasensitive and low consumption (estimated below 50 \(\mu\)W) piezotronic MEMS strain microsensors.

4:45pm AA1-Moa-14 Embedded Organics in Crystalline Fluorides: A One-Step Approach to Sensitized Luminescence, Per-Anders Hansen, University of Oslo, Norway; T Zikmund, Academy of Sciences of the Czech Republic, Czech Republic; T Yu, Utrecht University, Netherlands; J Nitsche Kvalvik, T Aarholt, Ø Prytz, University of Oslo, Norway; A Meijerink, Utrecht University, Netherlands; O Nilsen, University of Oslo, Norway

Photoluminescence, conversion of one type of light into another, allows turning blue LEDs into a warm white, enable molecular tagging, enhances optoelectronics and improves energy harvesting. The crucial point that decides if photoluminescence can tackle a given problem is the possibility to tune absorption, conversion and emission properties to the excitation source, required output wavelength and its efficiency. With the recent development of multi-step processes like down- and upconversion and the need to sensitize these with stronger absorption mechanisms, it is clear that optimizing all properties simultaneously is not possible within a single material class.

In this work, we have utilized the layer-by-layer approach of atomic layer deposition to combine broad absorption from an aromatic molecule with the high emission yields of crystalline multi-layer lanthanide fluorides in a single-step nanocomposite process. This approach results in complete energy transfer from the organic molecule while providing inorganic fluoride-like lanthanide luminescence. Sm\(^3+\) is easily quenched by organic sensitizers, but in our case we obtain strong fluoride-like Sm\(^3+\) emission sensitized by the strong UV absorption of terephthalic acid. This design allows combinations of otherwise incompatible species, both with respect to normally incompatible synthesis requirements and in controlling energy transfer and quenching routes.

5:00pm AA1-Moa-15 Atomic Layer Deposition of ZnO Quantum Dots for Optoelectronics, Jin Li, Ghent University, Belgium; Y Yu, X Bi, Beihang University, China

In the past few years, atomic layer deposition (ALD) has been recognized as a promising way in fabricating quantum dots (QDs). In principle, ALD growth would experience an “islands” period during the initial nucleation stage before forming a continuous layer. Therefore, by intentionally freezing the ALD process in the initial stage, quantum dots can be achieved instead of continuous layers. In contrast to other common QD synthesis methods such as solution-based processes, MBE or MOCDV, ALD can easily and precisely tune the chemical composition, size and spatial distribution of QDs at a much lower cost, as well as realizing functionalized coatings on nanoscale 3D architectures, which render it an excellent choice for implementing QDs in optoelectronic applications.

Herein, we report the study on ALD depositing metal-oxide QDs with ZnO as a model material, which is widely used in nanoscale optoelectronics.\(^3\)

The morphology evolution of as-deposited ZnO quantum dots by ALD, including the influence of the initial surface condition on the nucleation behavior of ALD, as well as the opportunity of using different plasma pre-treatment and buffer layers to improve the uniformity of nuclei distribution, which are of significance for QD deposition. Further, we demonstrated that precursor exposure time was an important factor in deciding the morphology of ALD QDs, which, in conjunction with ALD cycle number, lead to great freedom in adjusting the density and size of the QDs. In the present work, we realized monodisperse 2D QDs with average size tunable from 8.5 to 2.1nm. The QDs exhibited highly enhanced bandgap from 3.2 eV to 5.08 eV by controlling the growth conditions and exposure time was an important factor in deciding the morphology of ALD QDs. This approach results in complete energy transfer from the organic molecule while providing inorganic fluoride-like lanthanide luminescence. Sm\(^3+\) is easily quenched by organic sensitizers, but in our case we obtain strong fluoride-like Sm\(^3+\) emission sensitized by the strong UV absorption of terephthalic acid. This design allows combinations of otherwise incompatible species, both with respect to normally incompatible synthesis requirements and in controlling energy transfer and quenching routes.

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Reference

1. J. Li, Y. Yu and X. Bi, ACS Photonics, 2019, 6, 1715–1727.

Monday Afternoon, June 29, 2020
ALD Applications
Room Van Rysselberge - Session AA2-TuM
ALD for Batteries and Energy Storage I & II
Moderators: Arrelaine Dameron, Forge Nano, Neil Dagsupta, University of Michigan

9:00am AA2-TuM-3 Ultrathin TiN by Thermal ALD as Electrically Conducting Li-ion Diffusion Barrier for Integrated 3D Thin-Film Batteries, Jan Speulmans, A Kla, S Bönhardt, M Czernohorsky, W Weineich, Fraunhofer IPMS, Germany

Upcoming autonomous microelectronic devices for the Internet-of-Things require ultralow power consumption enabling on-chip energy storage. Integrated 3D thin-film batteries (TFB) are a promising solution to meet these demands [1]. Enhancement and an in-depth understanding of Li-ion diffusion barriers are crucial factors to enable these devices. The diffusion of Li-ions into the Si substrate would damage surrounding components, detach the battery, and lead to a loss of capacity.

Titanium nitride (TiN) is an excellent Li-ion diffusion barrier and current collector [2]. Thin films manufactured by plasma-enhanced atomic layer deposition (ALD) proved superior blocking properties compared to sputtered layers, e.g., the insertion of around 0.02 Li per TiN formula unit was achieved for a 32 nm thick film [3]. Additionally, a sufficient specific resistivity of 200 μΩ cm as a current collector was shown. Orientation with low surface energy and reduced film contents of oxygen and chlorine were key factors for the performance. However, the employed remote plasma ALD was challenging for a conformal coating of structured substrates. Further thickness reduction of the barrier could increase the active volume fraction in 3D TFB.

In this work, we compare ultrathin 10 nm TiN films by thermal ALD and pulsed chemical vapor deposition (pCVD). The depositions are executed at 400-450 °C using titanium chloride and ammonia as reactants. The ALD film demonstrates excellent blocking capability. Only 0.03 Li per TiN formula unit is inserted exceeding 200 cycles at 3 μA/cm² between 0.05 and 3 V vs. Li/Li⁺. The low specific resistivity of 115 μΩ cm allows the application as a current collector. In contrast, a partial barrier breakdown is observed for the 10 nm pCVD film. We identify that the surface quality is critical for the excellent performance of the ALD TiN. The superior surface is quantified by the lowest roughness, the highest ratio of the TiN-component, and the lowest Cl-content. Conformal deposition of TiN with thermal ALD is demonstrated in a newly designed electrochemical test chip with high aspect ratios of up to 20:1. First results of the barrier performance in 3D substrates are discussed.

10 nm TiN ALD films are an ideal candidate to enable increased energy density of integrated 3D TFB to power upcoming autonomous sensors.

References

9:15am AA2-TuM-4 Atomic Layer Deposition of Nitrogen Doped Al- and Ti-Phosphates for Li-Ion Battery Applications, Lowie Henderick, Ghent University, Belgium; H Hamed, University of Hasselt, Belgium; F Mattelaer, M Minjaew, Ghent University, Belgium; J Meersschaut, IMEC, Belgium; J Dendooven, Ghent University, Belgium; M Safari, University of Hasselt, Belgium; P Vereeeken, KU Leuven – University of Leuven/IMEC, Belgium; C Detavernier, Ghent University, Belgium

Phosphates have shown to be promising materials for Li-ion battery (LIB) applications. Their applications vary from protective coatings [Al-phosphate[1,2,3] to potential cathode materials (Ti-phosphate[4]). Using ALD to tune the ionic and/or electronic conductivity through in-situ N-doping could make these materials even more interesting. In order to, for example, decrease the ionic and electronic blocking effect of the protective Al-phosphate coating, a new plasma enhanced atomic layer deposition (PE-ALD) process has been investigated. This new process is based on reports on PE-ALD of metal phosphates using a combination of trimethyl phosphate solution (TMAP*), oxygen plasma (O²*) and a metal precursor (TMA or TIP*) [5].

In combining a nitrogen-containing phosphorous precursor, i.e. diethyl phosphoramidate plasma (DEPA*), with nitrogen plasma (N²*) and TMA/TIP*, a large GPC of 1.5 nm/cycle for N-doped Al-phosphate and 0.5 nm/cycle for N-doped Ti-phosphate was obtained. For both phosphates, self-limited growth is observed (figure 1, 2), and N-doping of respectively 7.9 at.% and 8.6 at.% for Al-phosphate and Ti-phosphate was found with Elastic Recoil Detection (ERD) (figure 3).

A clear effect of the nitrogen doping on the effective transversal ionic and electronic conductivities is observed (figure 4a). For both phosphates, a significant increase in the effective electronic conductivity is found. This is important, as phosphates (such as Fe-phosphate) typically suffer from poor electronic conductivity. The effective ionic conductivity shows a small increase for the Al-phosphate, but a slight decrease for Ti-phosphate. To study the possibilities of N-doped Al-phosphate in particular, a lithium nickel manganese cobalt oxide (NMC) powder was coated with (N-doped) Al-phosphate. An improved energy density at high discharge rates (w.r.t. uncoated NMC) was observed after only one deposition cycle of N-doped Al-phosphate, while the blocking effect of the undoped Al-phosphate coating (with a similar thickness as N-doped Al-phosphate) showed to hamper the battery performance at high rates (figure 4b). This shows that N-doping of phosphates with a high GPC was achieved by a new PE-ALD process, opening up opportunities for improving different types of phosphate coatings for LIB applications.


9:45am AA2-TuM-6 Passivation of Lithium Metal Anodes with ALD Aluminum Fluoride, John Hennessy, J Jones, K Billings, Jet Propulsion Laboratory

Lithium metal anodes are a key component of various next-generation battery technologies. However, the reactivity of the lithium surface can lead to battery cycling issues that are often associated with the formation of a solid electrolyte interphase (SEI) layer on the lithium surface. Here, we report on the use of ALD AlF₃ coatings deposited directly onto commercial lithium metal foils in order to engineer the stability of this SEI layer. ALD films are deposited at various substrate temperatures (< 175 °C) by cyclic exposure to tris(dimethylamino)aluminum and anhydrous HF. Symmetric Li/Li cells were fabricated with various electrolyte solutions in order to gauge the chemical stability of the passivated lithium surface. For example, electrochemical impedance spectroscopy reveals a significant reduction in the impedance growth of ALD-coated symmetric cells fabricated with a liquid electrolyte solution of LiPF₆ in acetonitrile. The AlF₃-coated Li was also fabricated to fabricate Li/S cells and more than doubled the specific capacity of test cells versus samples with unprotected Li. The increase in Li/S cell impedance during prolonged cycling was also reduced for the passivated samples, although not completely eliminated. Coated foils were also characterized with a combination of scanning electron microscopy, energy dispersive xray spectroscopy, and spectroscopic ellipsometry. Finally, progress in the development of lithium-ion conducting thin films of lithium aluminum fluoride is also presented as a building block toward solid-state battery systems.

10:15am AA2-TuM-8 Next-Generation Li-ion Batteries Enabled by Large-Area Atmospheric-Pressure Spatial Atomic Layer Deposition, Mahmoud Ameen, I Beeker, L Haverkate, B Anothurmakool, F Grob, D Hermes, N Huijssem, S Khandan Del, F Roozboom, S Unnikrishnan, TNO/Holst Center, Netherlands

Li-ion batteries have emerged as a key energy storage enabler, not only in portable electronic devices but also in electric vehicles and grid-storage. A combination of high energy density anodes such as Si or Li, and Ni- or Li-rich cathodes is necessary to achieve the targeted energy density (350 Wh/kg). However, many of such high-potential redox-chemistry lead to serious safety issues and degradation during cycling due to either oxidative or reductive instabilities, especially occurring at the electrode-electrolyte interface. Therefore, optimizing the interfaces with chemically and mechanically-stable Li-ion conductive passivation layers is crucial for any Li-ion battery chemistry in order to mitigate the non-compatibility of the individual cell components. The interfacial stabilization layers can be formed either in-situ using electrolyte additives or ex-situ via chemical and physical methods. One option here is offered by atomic layer deposition (ALD) which is the preferred technique to achieve superior quality and 3D-conformal coatings with atomic-scale thickness precision. However, conventional vacuum-based ALD is not compatible with the mainstream high-
throughput roll-to-roll battery electrode production. Here, the large-area atmospheric-pressure spatial-ALD (s-ALD) technology as established by TNO-Holst Centre several years ago can offer prime solutions for various applications including thin-film batteries. A wide range of materials like metal oxides, nitriles, sulfides, and hybrid organic-inorganic materials are possible using s-ALD. In this work, we will demonstrate several s-ALD films such as Al₂O₃, TiO₂, and ZnO which are specifically tailored for dendritic Li-growth suppression, interface stabilization, and cathode degradation protection. Furthermore, we will discuss the latest results on our upscalable s-ALD grown thin film LiPON electrolyte having a Li-ion conductivity >10⁻⁸ S/cm, low electronic conductivity (<10⁻⁸ S/cm) and high stability against Li-metal anode during cycling. Such electrolyte is also relevant for the development of protection layers in liquid and polymer electrolyte-based Li-ion batteries, as well as for enabling thin-film planar and 3D solid-state batteries with ultra-thin electrolyte layers.

References:

Tuesday Morning, June 30, 2020

Molecular Layer Deposition for Stabilization of Electrochemical Materials, Chunmei Ban, University of Colorado - Boulder

The inherent non-passivating behavior of electrode materials in the organic lithium-ion battery electrolyte results in large irreversible capacity loss and gradual electrolyte consumption during operation. Such interaction between electrolyte and electrode becomes more pronounced for intermetallic alloy and lithium-metal anode materials and high-voltage cathode materials. When using decreased nano-size electrode materials, the chemical interaction and the formation of solid electrolyte interphase (SEI) lead to even more irreversible loss of lithium inventory. Surface modifications on both active particles and laminated electrodes—with the capability to modify the surface and interface through the control of composition, thickness and mechanical properties—would chemically or physically change the surface of electrode materials. The atomic layer deposition (ALD) technique has proven itself to be the best method to deposit continuous, conformal and pinhole-free films. Our recent work has proven ALD as an important tool in mitigating the parasitic side reactions between the electrolyte and the electrode surface, which results in the greatly improved performance of lithium-ion electrodes. Furthermore, to address the challenge of dramatic volumetric change associated with high-capacity intermetallic anodes, we have used molecular layer deposition (MLD) to modify the surface with a mechanically robust, flexible coating. Coming along with the results from advanced characterization techniques, this talk will emphasize the unique chemical interaction between the electrolyte and the surface of intermetallic electrodes. Furthermore, the surface modification strategies will be introduced here and exploited, in order to dictate the interface chemistry and manipulating the chemical-physical properties of the electrode-electrolyte interphase for efficient electrochemical reactions.

References:

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The inherent non-passivating behavior of electrode materials in the organic lithium-ion battery electrolyte results in large irreversible capacity loss and
bandgap and possible growth of Zn$_{1-x}$Mg$_x$O films stacks with graded Mg doping. By achieving precise control of Mg content, we aim to investigate the effect of ALD grown Zn$_{1-x}$Mg$_x$O films on high-bandgap solar cells based on CuInS$_2$ absorbers.


10:00am AA-TuM-7 Tuning Properties of ALD Oxide and Sulfide Materials for Photovoltaic Applications, Nathanaelle Schneider, IPVF-CNRS, France

Atomic layer deposition (ALD) has unique capabilities that makes it very attractive to several applications and in particular photovoltaics (PV). It allows the deposition of pinhole-free thin films, in soft relative conditions (low temperature, low vacuum level), with finely tuned properties (thickness, composition, ...) and conformal on high-aspect-ratio and/or large surfaces. However, such fine tuning is rarely straightforward and simplistic view of monolayer per monolayer growth is never the case. This is crucial when growing thin films with more than two elements as specific surface reactions can impact the film growth. This is even more pronounced for sulfide multinary compounds due to the higher propensity of cation exchange, greater diffusion rates and unintentional annealing of the labile sulfur.

Such phenomena can be partly controlled by the right choice of precursors, adapting the order of precursor introduction or varying the number of successive growth cycles. A deep understanding of the surface chemistry is also necessary and can be achieved by combining modelling (DFT calculations), in-situ (such as quartz-crystal microbalance measurements) and ex-situ characterisations (XPS fine profiling, ...). The aforementioned unique ALD capabilities will be illustrated by examples in PV devices such as Cu(In,Ga)Se$_2$ and perovskite solar cells.


2 H. Le Tulzo, N. Schneider, and F. Donsanti, Materials 13, 645 (2020).


10:30am AA-TuM-9 Solar Cells Based on Phase-Pure Sb$_2$S$_3$ by Atomic Layer Deposition Forming Planar and Coaxial Heterojunctions, Ignacio Miguez Bacho, P. Böttner, F Scheler, D Döhler, Friedrich-Alexander-University Erlangen-Nürnberg, Germany; C Pointer, E Young, Lehigh University; J Bachmann, Friedrich-Alexander-University Erlangen-Nürnberg, Germany

Interfaces of oxides and heavier chalcogenides layers in thin-film or extremely thin absorber solar cells present defect states at the interface and often a chemical incompatibility which results in dewetting issues. Here, we establish atomic layer deposition (ALD) as a tool to overcome these limitations. ALD allows one to obtain highly pure Sb$_2$S$_3$ as light absorber layers, and we exploit this technique to generate an additional interfacial layer consisting of ZnS with thicknesses between 0.2 and 2.0 nm. This ultra-thin layer simultaneously eliminates dewetting, passivates defect states at the interface and slows down interfacial charge recombination. The ability of ALD to generate conformal coatings of porous substrates allows us to generalize the materials system from planar stacks to coaxial heterojunctions based on cylindrical nanostructures. In this system, we optimize length and layer thicknesses in dependence of the carrier diffusion lengths and the light absorption coefficient systematically. We achieve heterojunction solar devices with optimized power conversion efficiency beyond 5.0 %.

10:45am AA-TuM-10 Metal Oxide Infilling of Quantum Dot Thin Films: Charge Separation, Stabilization, and Solar Cell Formation, Fatemeh Hashemi, R Crisp, J Alkemade, G Grimaldi, N Kirkwood, L Siebbeles, J van Ommen, A Houtepen, Delft University of Technology, Netherlands

Colloidal semiconductor quantum dot (QD) thin films have various applications in photovoltaic devices and as light emitters. This is due to the controlled variation in their band-gap and ease of fabrication. However, these thin films suffer from instability due to their inherent inclination towards oxidative and photothermal degradation. Thus, to increase the stability of these materials for fabricating QD-based electronic devices, encapsulation or pore infilling processes are necessary. The pore infilling process has been shown to also enhance the conductivity and carrier mobility in the QD thin films. The encapsulation process should provide protection against oxidation without hindering the electron transport properties or causing sintering of the QDs. ALD is an ideal candidate for such a process as it provides excellent control over the growth in the sub-nanometer scale and results in conformal coating even in low temperatures.

We perform ALD of two different metal oxides in atmospheric pressure for the infilling and capping of QD thin films. We examine their effects on the stability and carrier mobility of the coated QD films. InP QDs are chosen because of their potential as light emitters (i.e. phosphors) across the visible spectrum. This is due to their favorable bandgap and high photoluminescence quantum yield. Furthermore, InP QDs exhibit multiple exciton generation allowing for higher solar cell efficiency than traditional materials. However, carrier mobility in QD films was too low for practical applications until now.

We compare the results of amorphous TiO$_2$ with crystalline ZnO films deposited with different thicknesses. The effects of the capping film thickness of QD film on stability and carrier mobility are studied with spectrophotometry and time-resolved microwave conductivity measurements. We show that the inorganic matrix reduces the size of tunnel barriers within the QD thin film hence increasing the carrier mobility through the film without causing sintering of the QDs. Furthermore, our results confirm that the quality of QD thin films is strongly improved when the inorganic ALD coating is applied. The ALD encapsulation process would open up the possibility of fabricating robust InP QD thin films for many optoelectronic devices.

11:00am AA-TuM-11 ALD of Al$_2$O$_3$ on Perovskite Solar Cells: Role of Active Interfacial Engineering, S Ghosh, N Mahului, Shabtal Sarkar, Indian Institute of Technology Bombay, India

Atomic Layer Deposition of ultrathin Al$_2$O$_3$ on hybrid perovskite solar cells drew significant attention due to the considerable improvement in the overall device stability. In our laboratory, with intermittent current-voltage measurements, the coated devices show the value of T80>7500 hours under ambient conditions. Subsequently, these coated devices are found highly stable when measured in a cyclic manner for 7 days, replicating the real-life day-night sequences. Such encapsulation is found very effective as an oxygen barrier-layer and water-impermeable membrane; hence contribute to the overall stability of these devices.

In this presentation, I would like to emphasize on our experimental findings, subsequently supported by device simulation, which undoubtedly reveals that the perovskite-spiroOMeTAD interfacial band-structure play a detrimental role in initiating the degradation processes in the pristine devices (device structure). We try to provide a comprehensive insight depicting an apparently non-trivial active phenomenon resulted due to the ALD grown Al$_2$O$_3$ layer that supposedly be a passive component of the entire device stack. Favorized electronic modification of the spiroOMeTAD/perovskite interface resulted due to the Al$_2$O$_3$ ALD provides better charge extraction and lesser ionic accumulation, unlike the unencapsulated devices, and hence offers better performance stability. Our study indicates that essentially the ionic accumulation triggers the device degradation that is eventually followed by materials degradation.
Photocatalysis has attracted much attention, due to its ability to degrade toxic organic compounds in wastewater into environmental friendly compounds such as CO₂ and water. Among the various photocatalytic materials, titanium dioxide (TiO₂) has been widely used due to its high photocatalytic efficiency, high stability and low toxicity. However, fast charge recombination and the narrow absorption range in the UV spectrum limit its photocatalytic efficiency under visible-light irradiation.

In this work TiO₂ nanofibers were synthesized by electrospinning method. In order to improve the photocatalytic activity under visible light, a developed process based on atomic layer deposition (ALD) was used to grow manganese oxide (MnOₓ) and palladium (Pd) on TiO₂. The morphological, structural and optical properties of all fibers were investigated by several characterization techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The influence of chemical and physical properties on the photocatalytic degradation of acetaminophen has been investigated. The results indicate that acetaminophen is stable and difficult to be photodegraded in the absence of photocatalyst. After 4h of visible light irradiation, acetaminophen has been degraded up to 90% in the presence of TiO₂-BN-Pd nanofibers, compared to only 20% degradation with pure TiO₂.

Based on these promising results, the development of ceramic nanofiltration membranes coated with these highly photocatalytic materials will be investigated. In parallel, a better understanding of the photocatalytic oxidation pathways (based on by-product analysis) coupled with toxicity tests (Vibrio Fisher, Microtox) will be studied.

**1:30pm AA-Tua-3 Atomic Layer Deposition of Manganese Oxide Ultra-Fine Clusters on Titanium Dioxide Nanoparticles for Photocatalytic Hydrogen Production: Experiments & Simulations, Saeed Saedy, R Verma, Delft University of Technology, Netherlands; S Rhugthon, University College Cork, Ireland; J Lu, Delft University of Technology, Ireland; M Nolan, University College Cork, Ireland; R van Ommer, Delft University of Technology, Netherlands**

Atomic layer deposition (ALD) is an attractive method to synthesize advanced functional nanomaterials e.g. photocatalyst: materials that use light to drive chemical reactions. ALD enables depositing uniform nanoparticles (NPs) on the support with controlled size, shape, and morphology. We have deposited manganese oxide (MnOₓ) ultra-fine clusters on titanium dioxide (TiO₂) NPs by means of a fluidized bed ALD reactor. Bis[ethylcyclopentadienyl]manganese ([η5-C₅H₅-C₂H₄]₂Mn) and hydroxylamine (NH₂OH) were used for ALD of MnO₂ clusters at 150°C. The microstructure and surface chemistry of ALD synthesized MnO₂/TiO₂ samples were examined using different methods including TEM, XPS, and XRD. The MnO₂/TiO₂ samples were employed as photocatalyst for solar production of H₂. In addition, we have performed first principles studies of models of MnO₂-modified TiO₂. We present detailed results on first principles modelling the metal precursor step in ALD of MnO₂ on TiO₂ substrates.

**2.45pm AA-Tua-8 Atmospheric-Pressure Atomic Layer Deposited Bimetallic MCo/CeO₂ Catalysts for Enhanced Removal of CO from Fuel-Cell Hydrogen by Preferential Oxidation, E Farmani Gheslaghi, A Trandoust, Fatemeh Gashoul, A Khodadadi, Y Mortazavi, University of Tehran, Iran**

Atomic layer deposition has recently been successfully used for uniform deposition of catalyst reactive species on supports with remarkable dispersion, intimate contact and stability. The hydrogen produced for PEM-fuel cells usually contains about 1% CO, which electrically poisons the fuel-cell. The CO can be removed at low temperatures by PROX.

Atomic layer deposition was used to deposit 2.3% Cu and either 0.3% Ni or 0.8% Ru on CeO₂ and the resulting bimetallic catalysts were used in preferential oxidation of CO in H₂-rich feed (PROX). Cu(acac)₂ was reacted with CeO₂–OH groups at 210°C for 75 min and the produced Hacac was monitored in a gas-cell in FTIR, followed by purging by Ar and subsequently introduction of zero-Air for oxidizing the remaining acac species at 350°C for 30 min. The number of CeO₂–OH groups was determined by Grignard reaction. The self-limiting deposition of (acac)Cu-CO₂-OCe was confirmed by monitoring Hacac FTIR peak at 1626 cm⁻¹. The density functional theory (DFT) results show that a range of manganese oxidation states can co-exist, along with oxygen vacancies and that the modification of TiO₂ with MnO₂ can enhance electron hole separation and trapping. Co-existence of Mn⁴⁺, Mn⁵⁺, and Mn⁶⁺ in heterojunction of MnO₂/TiO₂ facilitate charge separation and electron-hole trapping, resulting in superior H₂ productivity. The low temperature nature of ALD synthesis makes it possible to obtain good balance between these diverse oxidation states in final product; whilst the conventional wet chemistry methods require high temperature calcination step to remove the residues of precursors and solvent, which results in higher oxidation state of products as well as resulting in large particles.

**2.45pm AA-Tua-4 In situ Electrochemical APXPS Analysis of ALD Grown Cu Catalyst for CO₂ Reduction, H Ali-Löytty, J Palmolahi, M Hannula, Jesse Saari, Tapere University, Finland; K Lahtonen, Tapere University, Finland; H Wang, M Soldemo, A Nilsson, Stockholm University, Sweden; M Valden, Tapere University, Finland**

The grand challenge in artificial photosynthesis is to produce liquid solar fuels from water and carbon dioxide. Unfortunately, current materials solutions for a photocatalytic (PEC) solar fuel reactor lack efficiency, selectivity towards liquid fuel products, and long-term stability. Cu based catalysts are so far the most promising materials for the carbon dioxide reduction reaction (CO₂RR), whereas the selectivity of Cu catalyst towards liquid products is strongly affected by the exact chemical composition and structure. Recently, Elерт et al. suggested, based on in situ electrochemical APXPS measurements on Cu foil, that the high activity of oxide-derived copper towards CO₂RR stems from a lower surface oxygen that was proposed to increase the CO binding energy and thus enhance the production of methanol and multicharbon products [1]. This contradicts the alternative hypothesis that assigns the activity to CuO on the surface, albeit no copper oxide should be stable at reductive CO₂RR conditions.


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sharp decay of CO₂ produced in the oxidation step of remaining acac ligand was a further proof for self-limited deposition. The Catalyst average particle sizes are in the range of 8.7-13.4 nm. 2.3wt% Cu was deposited on ceria by ALD with a remarkable dispersion of 93% when 0.3wt% Ni was ALD deposited on the CuO/CoO; the dispersion is still very high at 84%, while the dispersion of the same NiCu/CoO catalyst prepared by the conventional method of impregnation is much lower at 66%. NiCu/CoO catalyst prepared by ALD reduces about 80-90 °C lower than the one prepared by impregnation, indicating higher oxygen mobility required for the PROX.

The CO conversion of catalysts in PROX is shown in Fig3. The lowest Tₙs and Tₜ₉₀ (i.e. temperatures at 50 and 90% CO conversion, respectively) were observed for RuCu/CoO. The NiCu/CoO catalyst prepared by ALD showed much higher activity corresponding to lower Tₙs and Tₜ₉₀ than the one prepared by impregnation. This catalyst showed a bifunctional synergy of chemisorption and activation of CO on Cu species and mars van krevelen oxidation using surface bimetallic nickel-copper oxide [1, 2]. In conclusion, the NiCu/CoO and RuCu/CoO catalysts prepared by self-limiting ALD method showed a remarkably high dispersion and activity in PROX.


3:30pm AA-Tua-11 ALD Fabrication of BN Membranes: Environmental Applications, Catherine Marichy, CNRS, France; W Hao, C Journet, V Sales, UNiv Lyon 1, France

INVITED

Boron nitride (BN) structures are very attractive materials with applications in various areas such as in energy and environmental domains. In particular, BN nanotubes (BNNT) have proven to be suited for conversion of osmotic energy. Use of nanotubes arrays or membrane would thus allow osmotic power harvesting under salinity gradients. BN nanostructures like foams and nanotubes have also revealed to be promising for water purification. ALD technique is an effective approach for surface modification and fabrication of complex nanostructured materials. Recently, based on the polymer derived ceramics route, we developed a two-step ALD process that enables using polymer template and fabricating various BN nanostructures.

Herein, the potential of ALD combined with PDGs for BN membranes will be discussed and exemplified. Highly stable boron nitride nanotube (BNNT) mats are fabricated, from low cost unwoven template, using the 2-step ALD of BN. The obtained membranes display high quality BNNTs, superhydrophobicity and stability over a month in air and various pH conditions. Thin material containing several thousands of BN tubes, are also prepared, from a commercially available membrane. In particular, using a double inversion of a polymer membrane combining ALD and PDC vapor infiltration, good quality and large surface boron nitride membranes are successfully elaborated with fine control of the through porosity in term of shape (from annular to cylindrical pores) and size (from few tens to hundreds nanometers). The ALD fabricated BN materials are characterized in term of morphology and structure using TEM, SEM, EDS, XPS and Raman. Particular attention is given to their use and performances in water treatment.


4:15pm AA-TUA-14 Highly Stable and Active Catalyst for Dry Reforming of Methane via Molecular Layer Deposition Approach, Piyush Ingale, C Guan, R Kraehnert, R Naumann d’Alnoncourt, A Thomas, Technische Universität Berlin, Germany; F Rosowski, BASF SE, Germany

Nickel based catalysts are typically used for the production of synthesis gas by reforming reaction. Dry reforming of methane (DRM) is an attractive reaction for production of synthesis gas by reduction of carbon dioxide. However, Ni nanoparticles (NPs) used in DRM reaction suffer from severe coking and sintering at high temperature which leads to decreased activity of the catalyst. The challenge is to synthesize a catalyst with a high Ni loading and dispersion that is stable under reaction conditions.

Molecular Layer Deposition (MLD) is a novel technique, which is a variant of atomic layer deposition. Organic compound replaces H₂O as ALD reactant to form purely organic or hybrid inorganic-organic layers. In our study, we deposited thin hybrid inorganic-organic layers of aluminate on NiO/SiO₂ catalyst via alternative reaction of trimethylaluminium and ethylene glycol at 150°C in a fixed bed reactor. The growth behavior of aluminate layers on NiO/SiO₂ powder was studied by in-situ mass-gravimetric study. The synthesized catalytic materials were analyzed by N₂ sorption, XPS, XRD, HRTEM and XRF. The reference and MLD modified catalysts were tested for activity and stability during dry reforming of methane at different temperatures (500°C-800°C). Deactivation of a Ni/SiO₂ reference catalyst was prevented by forming a defined porous net-like over-layer by decomposition of sacrificial organic part of aluminate, which prevented the sintering and detachment of Ni nanoparticles by filamentous carbon.

References

4:30pm AA-Tua-15 Using ALD to Probe Support and Promoter Effects for Synthesis Gas Conversion Catalysts, S Nathan, A Asundi, Stanford University; A Hoffman, A Bouvain, S Bare, SLAC National Accelerator Laboratory; Stacey F. Bent, Stanford University

With the intensifying global need for alternative energy and fuels, there is strong interest in the development of efficient catalysts that can drive the chemical conversion of renewable resources into useful products. One promising pathway is to catalytically convert synthesis gas (syngas, CO + H₂) to oxygenates. However, a commercial catalyst that converts syngas to desirable products such as ethanol and other higher oxygenates has not yet been developed due to the many kinetically favorable side reactions that shift selectivity away from the desired products. We study the conversion of syngas to synthetic liquid fuels using supported metal, heterogeneous catalysts. Two different examples will be described in which atomic layer deposition (ALD) is used to precisely-modify the catalysts to probe support and promoter effects. First, the promotion of rhodium-based catalysts, which have intrinsic selectivity towards desirable oxygenate production, is explored using metal oxides deposited by ALD to modify Rh nanoparticles with monolayer-precise amounts of MoO₃. We show that the promoted catalysts exhibit an increase in both activity and oxygenate selectivity relative to unpromoted Rh nanoparticles, and that this is the result of formation of a novel catalyst structure. The second system is cobalt-based catalysts. Recently, interest has risen in Co/C catalysts for oxygenate production. We will describe how introducing a ZnO promoting overlayer on Co/SiO₂ by ALD significantly enhances oxygenate selectivity by enabling Co/C formation during syngas reaction. By exploring several different metal oxide supports, we will show that the composition of the support surface strongly controls whether ZnO-promoted Co can transform into the catalytically-selective Co/C. Synchrotron-based studies provide insight into the mechanisms by which the support and promoters change reactivity, while density functional theory (DFT) calculations reveal the reaction pathways on the ALD-modified catalyst surfaces. The outlook for atomic scale surface modification using ALD to synthesize and study catalytic materials will be discussed.
AA-TuP-8 Stabilizing Red Fluoride LED Phosphors using Atomic Layer Deposition, R Verstraete, H Rijckaert, Geert Rampelberg, Ghent University, Belgium; E Coetsee-Hugo, M Duvenhage, H Swart, University of the Free State, South Africa; P Smet, C Detavernier, D Poelman, Ghent University, Belgium

Red fluoride phosphors, such as K2SiF6:Mn4+ [1-2], are now one of the key red components of white light-emitting diodes (wLEDs), e.g. in display backlighting. The [MnF6]3– complexes show a narrow luminescence band at 630 nm upon blue excitation, yielding saturated red emission in a spectral region in which the human eye sensitivity is still fairly high, which is an advantage over Eu2+ doped nitride phosphors.

Despite the excellent optical properties of many fluoride phosphors, a remaining hurdle is their moisture sensitivity. Hence, surface passivation of fluoride phosphors has been an important topic in recent literature [3-5]. Conventional passivation methods are based on wet chemical processes, potentially degrading the pristine material. Moreover, in heterogeneous core-shell approaches, the fluorine terminated surface of the core shows a lack of functional sites (e.g. hydroxy groups) inhibiting efficient bonding with typical shell materials.

In this work, the use of atomic layer deposition (ALD) for growth of Al2O3 and TiO2 seed layers on fluoride phosphor particles is investigated. The coated phosphors have hydroxy-saturated surfaces that are compatible for further bonding with hydrophobic shells. It was found that Al2O3 seed layers suffer from blistering, pore-formation and delamination. In contrast, conformal and uniform layers of TiO2 could be grown. Unlike the untreated phosphor, the TiO2 coated phosphor could easily be further treated with a hydrophobic shell [6].


AA-TuP-9 Modulated VO2 Phase Change Properties by Ge Doping, Guandong Bai, K Niang, J Robertson, University of Cambridge, UK

VO2 shows an abrupt phase change from insulating to metallic at ~ 68 °C. Because of this metal-insulator transition (MIT) property, we can make phase change switch with VO2. A functional random-access memory usually requires large device arrays and has a higher working temperature than 68 °C. Atomic layer deposition (ALD) has the advantage of good large area uniformity and conformality, therefore is suitable for memory applications.

To raise the VO2 transition temperature (TMIT), one method is doping. Among various dopants that have been investigated, Mg lowers the TMIT and Si shows mixed results, Ge is one of the few able to raise it.2,3 ALD can perform doping by inserting dopant cycles into vanadium precursor cycles, and the doping level can be fine controlled by varying the cycle number ratio. We used a Savannah ALD 100 system to deposit amorphous Ge-doped VO2 thin films, using tetrakis ethylmethylamino vanadium (IV) (TEMAV, heated at 105 °C) and germanium (IV) ethoxide (TEOGe, not heated) as the V and Ge precursor, respectively, and H2O (not heated) as oxidizer. The 4-inch Si/SiO2 substrates were kept at 150 °C during deposition. We addressed the low growth rate due to the low vapour pressure of TEMAy by developing multiple pulsing method to maximize the efficiency of the vanadium dose, reaching a growth rate of 0.6 A per cycle. The inserted Ge cycle number percentage varied from 0 to 10%. The as-deposited thin films are then crystallized by post-annealing at 450 °C in an Ar/O2 ambient in a quartz furnace.

We analyzed the properties of Ge-doped VO2 thin films at room temperature using spectroscopic ellipsometry (J. A. Woollam M-200), AFM, XRD (Bruker D8 DAVINCI), Raman spectroscopy (Horiba HR8000). We confirmed phase change property by checking resistivity on a Keithley 4200 parameter analyzer using a four-point probe measurement and varying the sample temperatures between 25 and 120 °C. Ellipsometry mapping shows good thickness uniformity across the 4-inch wafer. Raman spectra and XRD confirmed the +4 valency of vanadium. AFM images show a clear topography change as the Ge doping increases, grain size decreases and roughness increased from ~2.6 nm to ~5.2nm. Electrical measurement shows a decrease of MIT on-off ratio with the increase of Ge doping, from ~101 at undoped to ~102 with high Ge doping. However, TMIT increases from ~68 °C to ~78 °C, proving a modulated VO2 phase change property by Ge doping.


AA-TuP-10 Optical Fibers with TFBGs as Sensors, Eden Goodwin, D Mandia, S Barry, Carleton University, Canada

Tilted Bragg gratings in optical fibers through periodic changes to the core refractive index (RI) result in a reflection spectrum from the surface that permits interrogation of the surrounding refractive index (SRI). This sensitivity to the SRI has been used as sensor scaffold for biosensors and postulated as a mechanism exploitable for in-situ deposition sensing during ALD processes.

In order to monitor film growth in real time, two orthogonal modes of light are used: Transverse electric (TE)- and transverse magnetic (TM)-polarized. TE-polarized light creates an electric field in an azimuthal fashion that is parallel to the deposited film boundary at the fiber’s surface, while TM-polarized light creates an electric field radially, resulting in a field that is perpendicular. These different modes interact with the surrounding environment in drastically different fashion. Through in situ analysis of these two modes, we were able to observe the insulator-to-metal transition of ALD deposited gold from 4.2-5.5nm, demonstrating an optically conductive film. This was independently confirmed by four-point probe (4PP) measurements.

We also determined the SRI sensitivity of ALD deposited gold and alumina coated films of various thicknesses. The unprecedented level of sensitivity observed in gold coated fibers hold prospects for use in biosensing applications, particularly as a tool for optical aptasensors (biosensors utilizing single strands of DNA called aptamers) offering a cost effective, label free biomolecule detection method. This presentation will discuss the fabrication of a TFBG sensor as used in detection of gold metal deposition, and further discuss a framework for biosensing using gold-tethered DNA aptamers.

AA-TuP-14 Photocatalytic Lithography with Atomic Layer Deposited TiO2 Films to Tailor Biointerface Properties, Sofie Vandenbroucke, Ghent University - IMEC, Belgium; F Mattelaer, Ghent University, Belgium; K Jans, IMEC, Belgium; C Detavernier, Ghent University, Belgium; T Stakenborg, R Vos, IMEC, Belgium

Heterogeneous substrates with different functionalities are key for the production of micro- and nanostructures in various applications. For instance, the biointerface in biosensors and lab-on-a-chip devices comprise bioreceptor molecules specifically bound to the biosensor area to enable analyte detection, while an antifouling layer is deposited onto all other parts to prevent loss of the analyte by non-specific adsorption. Patterns of self-assembled monolayers (SAMs) are often used for these purposes, but a high-throughput production process that enables patterning on a large scale is not available.

In this work, direct photocatalytic lithography is used to generate a spatial pattern of an azido-containing SAM (N3-SAM) for the specific binding of biomolecules, and a polyethylene glycol SAM (PEG-SAM) in other areas to avoid non-specific binding. First, the degradation of N3-SAM is monitored as a function of UV exposure time for three different thicknesses. The 10 nm and 20 nm thick ALD TiO2 films are found to remove the hydrophobic C-chains and azido groups already after 3 min of UV exposure time, while the 5 nm thick films present very limited photocatalytic activity. X-ray diffraction measurements and a wet etching procedure shows that the activity is related to the crystallinity of the material as-deposited.
Next, a biofunctional pattern is successfully created using thin ALD TiO$_2$ films (≤ 20 nm) that are anatase-rich as-deposited, a conventional lithography mask and a short exposure time up to 5 min to a simple 308 nm UV-lamp. The effectiveness of this approach is visualized by coupling fluorescently labelled antibodies to the patterns. A schematic illustration of the patterning procedure and the resulting patterns can be seen in figure 1. It is found that the technique is very sensitive to the exposure time.

An exposure time of 3 min leads to printed features that are smaller than the pattern they are to be replaced. The feature size is limited by the undissolved ROS that etch their actual size on the photomask, but an incomplete removal of the N$_2$-SAM in the exposed areas due to the influence of the soda lime glass mask on the irradiation. A longer exposure time of 5 min on the other hand, can successfully remove all N$_2$-SAM from the exposed areas but results in some broadening of the printed features.

The patterning technique offers the opportunity to use such TiO$_2$ coatings for patterning inside the microfluidic channels of a lab-on-a-chip device as ALD is known for the uniform and conformal coating in high-aspect ratio features. In addition, the technique can be implemented in a high-throughput production environment as additional processing steps are limited and short UV exposure times can be used.

AA-TuP-15 Enhanced Activity and Selectivity of Co/Pl-Y-Al$_2$O$_3$ Fischer-Tropsch Catalyst by Atomic Layer Deposition Al$_2$O$_3$ Overcoat, Laura Keski-Kiviä, P Eskelinen, N Heikkinen, M Reinkainen, VTT Technical Research Centre of Finland, Finland; M Putkonen, University of Helsinki, Finland

Fischer-Tropsch synthesis is a widely used process where natural gas is converted to synthetic fuels by aid of metallic catalysts, e.g. cobalt. However, leaching, sintering and coke undermining the process by decreasing the activity and selectivity. Atomic layer deposition (ALD) provides a pathway to create an overcoat to protect active sites and stabilize the particles on the support. In our study, we used a Picosun R-200 ALD reactor with a POCA powder coating system to deposit thin Al$_2$O$_3$ overcoatings (TMA+H$_2$O, 15-40 cycles, 150 °C) on porous Co/Pt-Y-Al$_2$O$_3$ FT-catalysts. After deposition, we annealed the catalyst in N$_2$ at 420 °C. Catalysts were characterized by nitrogen adsorption-desorption with Brunauer-Emmet-Teller (BET), H$_2$-chemisorption, Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques. Catalytic performance was studied using a tubular fixed-bed reactor system.

Our FT catalyst with particular Al$_2$O$_3$ coating was remarkably more active than plain catalyst without overcoat. The number of cycles and annealing had a tremendous effect on catalyst properties. The catalyst with 35 cycles of alumina showed the highest activity, up to 53% without significant loss of selectivity towards heavier hydrocarbons (Figure 1). In addition, there was a noteworthy decrease in the olefin to paraffin ratio of light hydrocarbons. Based on our characterization, the altered catalytic properties result from the reformed surface structure of the catalyst and cobalt particle stabilization due to the annealed overcoating. The cobalt particle size decreased (XRD, chemisorption), surface area increased (BET) and roughening of the overcoated and annealed catalyst surface was detectable in the SEM images. We claim that these changes are due to the densification and a change of the composition of the overcoat, leading to a porous structure (with exposed) and new artificial active sites on the catalyst.

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AA-TuP-23 Ferroelectricity of Ferroelectric Hf$_2$Zr$_2$O$_7$/Antiferroelectric ZrO$_2$ Stack Structure Fabricated by Atomic Layer Deposition, Takashi Onaga, Meiji University, Japan; T Nabatame, National Institute for Materials Science, Japan; Y Jung, University of Texas at Dallas; H Hernandez-Arriaga, The University of Texas at Dallas; J Mohan, University of Texas at Dallas; H Kim, A Khosravi, The University of Texas at Dallas; N Sawamoto, Meiji University, Japan; C Nam, E Tsai, Brookhaven National Laboratory; T Nagato, National Institute for Materials Science, Japan; R Wallace, The University of Texas at Dallas; J Kim, University of Texas at Dallas; A Ogura, Meiji University, Japan.

It has been reported that Hf$_2$Zr$_2$O$_7$ (HZO) thin films show ferroelectric (FE) behavior over a wide Hf:Zr composition range, while pure HfO$_2$ and ZrO$_2$ layers generally exhibit paraelectric and antiferroelectric (AFE) behaviors, respectively. The characteristics of HZO/high-k stack structures, such as HZO/Al$_2$O$_3$, have been studied for the future memory device applications. However, it is still not clear how the AFE-ZrO$_2$ film affect the ferroelectricity of HZO film when the ZrO$_2$ is laminated with the HZO film. In this work, we studied the ferroelectricity and crystallinity of HZO/ZrO$_2$ (H/Z) stack structure fabricated using atomic layer deposition (ALD).

The TiN/HZ/Z/TiN capacitors were fabricated as follows: An HZO film was deposited on TiN bottom-electrode by ALD at 300 °C using (Hf/Zr)[N(CH$_3$)$_2$]$_2$(CH$_3$)(CH$_2$)$_2$ as the precursor. Subsequently, a HZO film was deposited at 300 °C using (CH$_3$)Zr[N(CH$_3$)$_2$]$_2$ and H$_2$O gas. This process was then repeated for 10 times. In this way, a TiN-electrode was fabricated by DC sputtering. Finally, post-deposition annealing (PDA) was performed at 600 °C for 1 min in a N$_2$ atmosphere. The capacitors with HZO/HfO$_2$ (H/Z) stacks and HZO single film were prepared as references.

For the grazing incidence X-ray diffraction (GI-XRD) patterns, the patterns of the Zr/H/Z case showed the peaks from paraelectric monoclinic (M) phase. On the other hand, the peak from FE-orthorhombic, tetragonal, and cubic (O/T/C) phases was observed for the H/Z case, while those from M phase were suppressed, indicating that the H/Z stacks consisted mainly of O/T/C phases. For the polarization-electric field (P-E) curves, the H/Z stacks showed paraelectric properties regardless of the HZO thickness. On the other hand, the P-E loops of the H/Z stacks changed from AFE to FE behavior as the HZO thickness increased. Therefore, the remanent polarization (P$_R$) of the H/Z stack gradually increased with the HZO thickness, while the P-E loops of the HZO layers were small. The pure ZrO$_2$ film can exhibit FE behavior. Thus, these results suggest that the ZrO$_2$ films could exhibit FE properties as the HZO thickness increased. In conclusion, the properties of the H/Z stacks changed from AFE to FE behavior as the HZO thickness increased, which indicates that the ZrO$_2$ film of the H/Z stack could exhibit FE properties.

This work was partially supported by JSPS KAKENHI (JP18J22998).


AA-TuP-24 Study on Optical and Electrical Properties of Zn(O,S) Films Deposited by Atomic Layer Deposition (ALD), N Koothan, Yu-Hsuan Yu, C Kei, W Cho, T Chou, Taiwan Instrument Research Institute, Republic of China

Zn(O,S) is considered to replace CdS buffer layer in CIGS photovoltaic devices to avoid the use of toxic Cd. The efficiency of solar cells can be improved with the ideal conduction band offset (CBO), which can be optimized by adjusting the composition ratio between oxygen to sulfur. The buffer layer in CIGS requires full coverage with a pore-free, uniform layer. Therefore, ALD is adapted to deposit Zn(O,S) because it offers precise thickness control and conformal coverage.

A home-built ALD system was used to grow Zn(O,S) films, where Diethylzinc (DEZ), H$_2$O and H$_2$S were used as a metal source, oxygen source and sulfur source respectively. The ZnO ALD cycle sequence is 0.2 s DEZ, 0.1 s of H$_2$O separated by 10 s of N$_2$ purge, whereas, the ZnS ALD cycle sequence is 0.2 s DEZ, 0.1 s of H$_2$S separated by 10 s of N$_2$ purge. Fig.1 shows a supercycle in deposition progress of Zn(O,S), where m number of ZnO cycle and n number of ZnS cycles were deposited alternately. Zn(O,S) films with different ratios of m:n (ZnO:ZnS) such as 3:1, 5:1, 7:1 and 9:1 were fabricated in this study. The composition analysis of Zn(O,S) films was done by XPS. The optical and electrical properties were measured by UV-visual spectrophotometer and Hall measurement, respectively.

The Zn(O,S) films were deposited at 200°C with a growth rate of 1.6 Å/cycle for ZnO and 1 Å/cycle for ZnS. TEM results in Fig. 2 showed that the Zn(O,S) films can be fabricated by ALD with good conformality. Absorbance in Fig.3 shows that the absorbance of Zn(O,S) was larger than pure ZnO and ZnS within visible light wavelength.

AA-TuP-25 Atomic Layer Deposition of Highly Dispersed Manganese Oxide on Mesoporous Silicon Oxide for Selective Catalytic Reduction of Nitrogen Oxides, Saeed Saedy, Delft University of Technology, Netherlands; D Urbanas, P Baltruanas, Vilnius Gediminas Technical University, Lithuania; R van Ommen, Delft University of Technology, Netherlands

Atomic layer deposition (ALD) is a reliable method to produce catalysts in a highly controlled manner. The low temperature nature of ALD makes it possible to obtain different metal oxide nano-coatings at temperatures.
considerably lower than what is required to obtain the final product using conventional wet chemistry methods. Selective catalytic reduction of nitrogen oxides using ammonia (NO, NH3-SCR) is demonstrated as the most efficient NOx abatement technology among different NOx removal methods. The commercially available NH3-SCR catalysts suffer from high temperature operational condition, i.e. 300-450°C. This requires the catalyst bed to be insulated or deactivation and dual removal until this issue. The catalysts do not deactivate by sulfur-containing compounds and dust. Manganese oxide (MnOx) catalysts have a superior NH3-SCR activity at temperatures lower than 250°C; the low temperature SCR activity of MnOx catalysts is attributed to the excellent redox ability of MnOx and the various oxidation states of manganese (Mn2+, Mn3+ and Mn4+) which are necessary to complete the NH3-SCR reaction cycle. Since crystalline MnOx does not contribute effectively to NH3-SCR, the dispersion of MnOx strongly affects the LT SCR activity. Accordingly, the conventional methods of catalysts synthesis, e.g. precipitation and impregnation, are not suitable for preparation of MnOx-based SCR catalysts, because they often fail to achieve highly-dispersed supported nanoparticles (NPs). These methods usually require high temperature post-treatment resulting in improved crystallinity of NPs and decreased dispersion.

In this work we have employed fluidized bed ALD for deposition of highly dispersed MnOx on mesoporous silica (m-SiO2) aiming at low temperature NH3-SCR catalyst. The ultra-fine MnOx NPs were deposited on m-SiO2 at 150°C and 1 bar. The XPS spectra of ALD-synthesized MnOx/m-SiO2 catalysts revealed three oxidation states of Mn2+, Mn3+ and Mn4+ in these samples. However, powder XRD was not able to detect any crystalline phases of MnOx, suggesting that the crystalline MnOx phase is avoided via ALD synthesis; consistently, the MnOx NPs were scarcely observable using TEM imaging. This suggests extreme dispersion of MnOx over m-SiO2. The changes in surface area of support before and after ALD of MnOx measured using BET method, was also negligible (ca. 448 m2·g-1); this indicates that MnOx is highly dispersed over support without pore clogging. The obtained MnOx/m-SiO2 with such characteristics provide a promising catalyst for low-temperature selective catalytic reduction of nitrogen oxides.

AA-TuP-26 Effect of Deposition Temperature on the Crystallinity and Polarization of Ga-doped HfOx Films by Atomic Layer Deposition, Ju-Young Jeong, Ho Sohn, Y Han, Yonsei University, Republic of Korea

Ferroelectric random access memory (FRAM) is considered as one of next generation memory devices due to its merits such as low power consumption and high data transfer speed. Recently, HfOx thin films with non-centrosymmetric orthorhombic phase of the space group of Pn21, attracted intensive attention because of their ferroelectric property. Also, effects of doping, stress, and substrate were studied to enhance the ferroelectricity of HfOx films. [2] It was reported that the ferroelectric behavior of HfOx was affected by conditions such as deposition and post annealing temperatures in addition to alloying elements.[2]

In this study, Ga-doped HfOx (Ga-HfOx) films were deposited at various temperatures, ranging from 300°C to 340°C. Ga-HfOx films were grown on bottom electrodes of TiN by atomic layer deposition with Tetrais(ethylmethylamino)-halium(TEMA-HI), Trimethyl-gallium (TMG) as precursors and ozone as the oxidant. Then, top electrodes of 15nm-thick TiN were deposited by sputtering. And the post annealing was conducted by rapid thermal annealing (RTA) in N2 atmosphere at 600 °C during 20s.

Chemical composition and bonding of Ga-HfOx films were investigated by X-ray photoelectron spectroscopy (XPS). Structural properties were examined by Grazing Incidence X-ray diffraction (GI-XRD). The ferroelectric behaviors of Ga-HfOx films were measured by P-V, PUND methods with electric pulses of 3.3 MV/cm at 50 kHz and the endurance of ferroelectric switching, in addition.

Ga concentration and the non-lattice oxygen in Ga-HfOx film were estimated to be 5.9 % and 17. 2 %, respectively. GI-XRD shows an increased intensity in nano-crystalline peak with increasing deposition temperature. But the remanent polarization of Ga-HfOx film was decreased with increasing deposition temperature.

Acknowledgments

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References


AA-TuP-27 Low Damage Remote Plasma ALD of Dielectric Layers on Graphene, Michael Powell, Oxford Instruments Plasma Technology, UK; B Canto, M Otto, S Kataria, AMO GmbH, Germany; A O’Mahony, O Thomas, Oxford Instruments Plasma Technology; H Knoops, Eindhoven University of Technology, Netherlands; D Neumaier, M Lemme, AMO GmbH, Germany; R Sundaram, Oxford Instruments Plasma Technology

As electronic devices become ever smaller and with the push for greater efficiency, 2-dimensional materials are becoming increasingly more desirable. Amongst 2-D materials, graphene is one of the most widely researched - this is due to the extraordinary charge carrier concentration and mobility of the electrons in this material. Although graphene is excellently suited for a wide range of applications, it requires the deposition of both dielectric as well as encapsulation/barrier layers, to modulate the electrical response from the graphene as well as physically protecting it from damage.

ALD is a technique that allows uniform and precise control of dielectrics, deposited by a soft/low damage route. Thermal ALD processes, unfortunately, often suffer from poor nucleation when deposited on graphene and also poor adhesion of dielectric layers deposited on graphene. This presents challenges, as graphene is susceptible to damage by both radicals/ions as well as high temperatures, meaning that many routes to depositing these dielectric/barrier layers can result in poor device quality.

We will describe how short, low power remote plasma processing can result in high quality and conformal Al2O3 dielectric layers deposited on graphene surfaces with low damage, as demonstrated by ellipsometry maps and Raman spectroscopy (fig 1). We will further show that by utilising a stacked structure, where h-BN is incorporated between the graphene and alumina layers, damage is further reduced to the graphene during deposition. We will demonstrate that these layers have good electrical properties with high throughput/processing times; which is essential for scaling graphene devices for industrial processes. Furthermore, plasma processing of the dielectric layers allows thermally sensitive substrates to be used for device construction further expanding the scope for device construction.

References:


AA-TuP-30 Design of Li-Containing Layers with LiHMDS, Andreas Werbroeck, F Mattelaer, T Dobbelare, M Minjauw, Ghent University, Belgium; F Munnik, J Julin, Helmholtz-Zentrum Dresden-Rossendorf, Germany; J Dendooven, C Detavernier, Ghent University, Belgium

ALD will be a key technique for solid electrolyte applications and protective films on Li-ion battery electrodes. Its conformity, uniformity and thickness control are key selling points no other technique can match. While a lot of simple oxides can be deposited for battery applications, battery performance could greatly benefit from the further development of lithium-containing processes.

Lithium hexamethyl disilyl azide (LHDMDS) is one of the few precursors suitable for the atomic layer deposition of lithium-containing layers. Earlier results with LiHMDS which are relevant for solid electrolyte applications are the growth of lithium silicate with O2·2, crystalline Li2PO4 with trimethylphosphite (TMP)3 and amorphous LiPON with diethyl phosphoramidate (DEPA)4 as a reactant. From the literature it is clear that in some cases LHDMDS exhibits a dual source behavior, incorporating lithium as well as silicon in the films, while in other processes it only deposits lithium.

We developed a new, simple ALD process to deposit lithium silicate with LiHMDS and O2 plasma. The films were characterized with in-situ
ellipsometry, ERD and XPS (figs.1 and 2). Lithium and silicon are both present in the deposited films.

With the aim of depositing a lithium silicate/phosphate, we intermixed the LiHMDS-O$_2$\* process with TMP in an ABC/ACB way. These processes were as well self-saturating, and the stoichiometry of the resulting films was measured by XPS/ERD.

Recently we developed a new way to conduct mass spectrometry\(^\text{1}\). Our method allows to obtain a measurement of all masses as a function of time during a full ALD cycle (fig. 3). This way the reaction products arising in an ALD process can be fingerprinted and identified. We employed this method to the new LiSiO$_2$ process with O$_2$ plasma, the known Li$_2$PO$_3$ process, and the LiHMDS$/O_2$/TMP and LiHMDS/TMP/$O_2$\* process.

The composition of the films deposited with these mixed processes combined with the mass spectrometry measurements provided us with more insight in the dual-source behavior of LiHMDS and how it is affected by the preceding and succeeding precursor.


### AA-TuP-32 Resistive Switching in Titanium-Aluminum-Oxide Thin Films Grown by Atomic Layer Deposition, Joonas Merisalu, T Arroval, A Kasikov, K Kukli, A Tamm, J Aarik, University of Tartu, Estonia

Resistive switching (RS) phenomena in solid thin solid films have gained a lot of interest during the last decade offering potential for fabricating a new generation of non-volatile memory devices named resistive random access memories (RRAMs)\(^[1]\).

As there are a lot of materials discovered with resistive switching properties, the explanation of RS mechanisms is complicated\(^[2]\). Intense research is going on and devoted to the modifications of the RS media, together with the interpretation of their electrical characteristics obtained from various metal-insulator-metal (MIM) structures. In the present work, electrical characteristics of RS in titanium aluminum oxide thin films are studied.

The electrically evaluated samples have MIM structure which differ from each other by the titanium-aluminum oxide multi-layer insulator film construction. All the films were deposited on Si substrate pre-covered with RuO$_2$ layers that acted as common bottom electrode. The insulator layers were prepared by atomic layer deposition at 350°C from TiCl$_4$, Al(CH$_3$)$_3$, and H$_2$O.

The dielectric is a thin film containing layers of TiO$_2$ and Al$_2$O$_3$, was constructed by varying ordinarily deposited TiO$_2$ layers with the layers of TiO$_2$, which were deposited as a triple precursor process. This means that the pulse of titanium precursor was followed by aluminum precursor pulse and, then, the formation of oxide layer in a single cycle was completed by application of oxygen precursor, H$_2$O pulse. The growth rate of reference TiO$_2$ layers was 0.05 nm/cycle\(^[3]\). The growth rate of TiO$_2$:Al$_2$O$_3$ layer was 0.15 nm/cycle\(^[4]\). The atomic ratio Al/(Al+ Ti) was 0.6 [4].

The top electrodes of Pt were deposited through a shadow mask using electron beam evaporation.

Electrical charactereristics were measured as voltage sweeps using Cascade Microtech EPS-150 probe station and Keithley 2636A. All studied samples showed bipolar RS properties. Clockwise bipolar RS was recognized dominantly in samples where Al$_2$O$_3$ concentration was lower. The samples that contained more Al$_2$O$_3$ tended to show signs or even full repetitive cycles of counterclockwise RS. It was also noticed that R$_{LRS}/R_{HRS}$ ratio between low resistance state (LRS) and high resistance state (HRS) became higher when there was more Al$_2$O$_3$ present in the film.

### REFERENCES


### AA-TuP-34 New Hydrazine Based Precursors For Semiconductor Fabrication, Wolf Schorn, O Brief, R Karch, Unimicro AG & Co. KG, Germany; W Stolz, NAsP III/V GmbH, Germany

Continuous scaling of semiconductor devices sometimes can only be achieved by introducing new materials with improved properties. CVD and ALD processes are increasingly used to meet required film conformalities of complex three-dimensional structures exhibiting specific electrical properties.

A new class of substances has proven to be a potential candidate for ALD/CVD processes, metal complexes based on the ligand N,N'-bisdimethylaminocetamide (Hbdma), whose properties combine high volatility with high reactivity. In addition, this class of ligands can be used to prepare complexes where the metal cations are solely surrounded by hydrogen and nitrogen atoms aiming at minimizing unwanted carbon impurities in deposited films.

We present various Group III complexes based on the bdma ligand, their thermal characterization, as well as first deposition tests with the complex [Ga(bdma)H$_2$]. Furthermore, Bdma is a versatile ligand which can stabilize and volatilize many metal complexes based on main group elements such as Ge or B as well as transition metals such as Ni or Fe. Herein we wish to give an outlook of further work in progress.

Literature:


### AA-TuP-39 The Use of ALD Layers for Hermetic Encapsulation in the Development of a Flexible Implantable Micro Electrode for Neural Recording and Stimulation, David Schaubroeck, IMEC - Ghent University, Belgium; C Li, Ghent University - IMEC, Belgium; R Verplancke, D Cuypers, M Cauwe, M Op de Beeck, IMEC - Ghent University, Belgium

The use of electronic microsystems as medical implants gains interests due to the combination of superior device functionality with extreme miniaturization. Electronic devices are not biocompatible and will suffer from corrosion, hence a very good hermetic device encapsulation is of utmost importance. The hermetic sealing of implantable electronics requires extremely good bi-directional barrier properties against diffusion of water, ions and gases. Moreover, extremely long biostability against body fluids and biomolecules is an important requirement for the barrier materials. In this work, an ALD multilayer of AlOx and HfOx in combination with flexible polyimide is used as a flexible hermetic encapsulation of an electronic CMOS chip which serves as an implantable probe (so called hdtIME (active high-density transverse intrafascicular microelectrode)) probe for neural recording and stimulation\(^[1]\). The main part consists of a 35µm thin polyimide chips with electrodes on top encapsulated with alternating layers of spin coated polyimide (PI2611) and biocompatible ALD layers.

The total encapsulation is developed to provide excellent barrier properties. Each ALD stack (ALD-3) consists of AlOx (20 nm) capped on both sides with HfOx (8 nm) to avoid hydrolysis of AlOx. The ALD deposition temperature is 250°C. Special attention is paid to the adhesion of the ALD layers toward polyimide and vice versa. 3 to 4 PI/ALD-3 dyads are used for the total encapsulation, since long term implantation of the medical device is envisaged. Testing however is done using only a part of the total encapsulation, in order to enable to learn about the barrier properties in a reasonable timeframe. The WVTR of a PI/ALD-3/PI film reached a value of 2.1 $10^2$ g/m²day (38°C and 100% RH), the total encapsulation with 3 to 4 dyads will lead to WVTR’s in the order of $10^3$g/m²day. The same PI/ALD-3/PI film has been deposited on structured copper meanders and is exposed to PBS at 60°C for 3.5 years (equivalent to 17.5 years at 37°C)\(^[2]\). Up till now, no change in Cu resistivity has been observed proving the excellent barrier properties of the PI/ALD-3/PI film.

\(^[1]\) Rik Verplancke et al., 2020 J. Micromech. Microeng., 30, 015010

\(^[2]\) Changzheng Li et al. 2019 Coatings, 9, 579
The effect of electrode material and doping concentration on physical and electrical properties by using thermal and plasma-assisted atomic layer deposition in ferroelectric Zr-doped HfO2 dielectrics, P. Juan, Ming Chi University of Technology, Republic of China; Wen-Hao Cho, Taiwan Instrument Research Institute, Republic of China; C. Chen, National Applied Research Laboratories, Republic of China; C. Kei, Taiwan Instrument Research Institute, Republic of China.

Zr-doped HfO2 films with TiN and/or TaN as the metal electrode for sandwich-like metal-insulator-metal capacitors were fabricated. The Zr-doped HfO2 layers i.e., Hf1-xZr0.2O2, Hf0.75Zr0.25O2, Hf0.5Zr0.5O2, Hf0.25Zr0.75O2 were designed by the stacking of HfO2 and ZrO2 thin-films using the thermal and plasma-assisted atomic deposition (ALD). The precursors used for HfO2 and ZrO2 depositions were TEMAH and TEMAMr with water vaporizing and oxygen ambient, respectively. The thicknesses per cycle obtained from the converged regime are 0.112 nm/cycle for thermal and 0.117 nm/cycle for plasma in HfO2 films, respectively. While the thicknesses per cycle obtained are 0.111 nm/cycle for thermal and 0.118 nm/cycle for plasma in ZrO2 films, respectively. Each sub-stacked layer of same atomic species was fixed to 5 cycles and the total thickness of Zr-doped HfO2 was controlled to 20 nm. From the XRD patterns, the dielectric film is easier to be crystallized at post-annealing temperature of 450°C for thermal than that of 600°C for plasma. The intensity of tetragonal phase increases with increasing the doping amount of Zr for both thermal and plasma conditions. Secondary phases of TaO and Ti2ZrO4, are shown with TaN and TiN as the electrodes in thermal, but only Ti-related phase is observed in plasma scheme. The electrical properties of current-voltage and capacitance-voltage are measured and compared. A subthreshold voltage is severely shifted and the subthreshold slope is worse for samples with thermal condition. It indicated that high interface densities between dielectric film and silicon substrate is suggested and quantified by the conduction method. In a low doping concentration of Zr, the behavior of ferroelectricity is attributed to the formation of a non-centrosymmetric orthorhombic phase of space group Pbc21, which was found in the presence of TiN for plasma and TaN for thermal conditions.


The transfer of the principles of atomic layer deposition (ALD) is possible in the liquid phase. The precursors are dissolved in a solvent and they are sequentially injected in a microfluidic chamber. This is also a generalization of already established methods such as the ‘layer by layer’ growth or the ‘successive ion layer adsorption and reaction’ (SILAR). Solution ALD (sALD) shares the fundamental properties of standard gas ALD (gALD), specially the self-limiting growth and the ability to coat porous structures. In the following the targeted field is photovoltaics. A great deal of interest has appeared on a new generation of material for solar cell applications. Among them the perovskites are particularly interesting and the most studied one is CH3NH3PbI3 (MAPI). The existing deposition methods such as spin coating or vapor-deposition techniques do not allow a control at the atomic level. ALD has been used to deposit PbS but it needed a two-step conversion method to obtain a perovskite [1]. Therefore, a new process based on SALD has been developed to deposit PbI2. It allows the use of inexpensive lead salt and it is easy to process. Then, the PbI2 can be easily converted to MAPI. The PbI2 deposition is achieved with Pb(NO3)2 and Li via s-ALD on large samples (up to 10 cm×10 cm). The ALD behavior is shown from the linear dependency the thickness in function of the number of cycles as well as from the saturation curves. The influence of the deposition parameters on the morphology, the crystalline structure and the chemical composition are investigated by scanning electron microscopy, atomic force microscopy, grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy. The growth of PbI2 has been studied on different oxides with different chemical pre-treatment. Later, the obtained PbI2 is converted to MAPI by vapor annealing. The influence of the temperature, the time and the type of gas on the conversion are investigated on the different substrates. Furthermore, the influence of the ALD parameters on the properties of the perovskite layer were studied. Thus, the Perovskite layer has been integrated into a solar cell.

was observed that TiN crystallites become very small at increased Si,N, content (Figure 2). Thus, under mechanical loading the material only reacts by grain boundary sliding which requires more energy than deformation by dislocation movement, therefore, higher hardness is achieved. At high Si-dose, the mean grain separation becomes so wide, that cracking takes place in Si,N,matrix, thereby reducing the hardness. Additionally, control of Si,N in the Eugenis Ti-Si-N film enables tuning of the morphology from polycrystalline to fully amorphous with optimum resistivity; in all cases, excellent step coverage on high aspect ratio structures were obtained.

AA-Tup-61 The Influence of ALD-ZnSnO Buffer Layer Process Conditions on the Characteristics of TiN Sulfide Thin Film Solar Cells, Jae Yu Cho, J Heo, Chonnam National University, Republic of Korea
Choice of suitable n-type buffer layer to form favorable heterojunction is one of the promising criteria to achieve a high performance thin film solar cell (TFSC). Till date, CdS has been used as standard buffer layer for various TFSCs. However, the Cd-free alternative buffer layers are always in demand to increase environmental compatibility of such TFSCs. In this regard, atomic layer deposition (ALD) has already been proven as a potential technique to obtain conformal and ultrathin buffer layers.

In 2014, ~4.36% efficiency of SnS TFSCs with ALD-Zn(0,S) buffer layer has been reported by R. G. Gordon group, which is the best SnS TFSCs reported so far [1]. In this work, the application of ALD-ZnSnO (ZTO) buffer layer was investigated for SnS TFSCs. Initially, ZTO films were characterized for variable process conditions. Finally, the performance of the TFSCs was tested with ALD-grown ZTO buffer layers and the highest efficiency of 4.93% was achieved with the Voc = 436 mV, Jsc = 24.0 mA/cm², and FF = 0.47. The detailed analysis of the influence of ALD conditions on the device performance will be presented.

AA-Tup-64 Innovative ALD Industrial Services, Joël Mattheby, P Steinmann, L Steinmann, B Steinmann, Positive Coating SA, Switzerland
Positive Coating provides thin-film coating services based on magnetron sputtering and atomic layer deposition technologies. Combining the benefits of both processes, the company is mainly active in the luxury sector. Positive Coating is the pioneer that has brought ALD within the Swiss watchmaking industry as early as 2014. Heading now for diversification, Positive Coating makes its knowledge and expertise available to other industrial applications. Based on innovation and quality, it stands as a partner to develop custom-made activities related to surface engineering. New challenging applications in the medical field will be addressed. In the presentation, two patented processes will be discussed. Firstly, a unique method to produce two-tone components without organic masking. Secondly, a ultra-white coating that combines electroplating and ALD technologies. Finally, commercial applications and examples will be presented.

AA-Tup-66 Antireflection Coating on PMMA Substrates by Atomic Layer Deposition (ALD), Pallabi Paul, Friedrich Schiller University, Germany; K Pfeiffer, Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany; A Szeghalmi, Friedrich Schiller University, Germany
Atomic layer deposition (ALD) is a promising chemical coating technology for growing conformal films on high aspect ratios as well as complex shaped substrates. ALD is a cyclic process, which is based on sequential and self-limiting reactions of precursors with the available functional groups on substrate surface. In contrast to conventional physical vapour deposition (PVD) methods where shadowing may occur on strongly curved surfaces leading to thickness gradient, ALD can produce uniform and conformal films on arbitrarily shaped surfaces due to the self-saturating surface reactions and precise thickness control at the nanometer range. Thermoplastics like poly(methyl methacrylate) (PMMA) has been widely used in producing various optical components like freeform surfaces, aspheric lenses, Fresnel lenses and many other diffractive optical elements. PMMA has a high transmission in the visible spectral range, excellent hardness and high Abbe number enabling it as an important alternative to PMMA. Since the optimized process on PMMA dome ensuring identical spectral response along the entire dome surface. These investigations enable a possible route by ALD to deposit uniform, crack-free, adhesive and environmentally durable thin film layers on sensitive thermoplastics like PMMA.

References:
1. Paul et al., Coatings 2020, 10(1), 64.

As design rule of semiconductor device decrease continuously, various high-k materials have been evaluated including ZrO2, HfO2, TiO2, and (Ba,Sr)TiO3 [1-5]. Among of them, ZrO2 is the most commonly used as a dielectric material of capacitor in DRAM (Dynamic Random Access Memory). However, it was difficult to develop high quality ZrO2 process in 3-dimensional structure because ZrO2 ALD (Atomic Layer Deposition) didn’t show an ideal behavior.

In this study, we investigated deposition behavior of ZrO2 ALD using 1:1 mixture [TEMAZ+EMA] of TEMAZ ([EthylMethylAmino]Zirconium) and EMA ([EthylMethylAmine]. TEMAZ+EMA showed 20°C higher thermal stability and 10°C higher decomposition temperature than those of TEMAZ. The thermal stability of precursors is related to the number of effective electron around the central metal. It is assumed that TEMAZ+EMA precursor is stabilized because Zr atom in the precursor is coordinated by EMA and the number of effective electron around Zr atom increase.

We compared electrical characteristics of the TiN/ZrO2/Ti capacitor using TEMAZ and TEMAZ+EMA. The leakage current density and Schottky barrier heights were significantly improved at ZrO2 films deposited using TEMAZ+EMA. We will present the correlation between physical properties of precursors and electrical properties of ZrO2 films.

References:

AA-Tup-70 Mechanism of Leakage Variation with Aspect Ratio in ALD High-k ZrO2 and HZO Dielectrics, Martin McBrierty, R Clarke, S Barabash, K Littau, Intermolecular
DRAM capacitors require ALD of ultrathin high-k dielectrics, such as ZrO2 or (Hf,Zr)O2 (HZO), throughout high aspect ratio (HAR) features. However, device performance may be compromised by trap states and other defects due to non-ideal ALD at high aspect ratios, constraining achievable capacitance. We demonstrate a simple, low-cost lateral high aspect ratio (LHAR) platform to link material properties, ALD process parameters, and device performance as a function of equivalent aspect ratio. Metal-insulator-metal capacitor (MIMcap) structures were prepared with physical vapor deposited ALD Ti electrodes and ALD ZrO2 or HZO dielectrics grown in the LHAR test structure using metal-organic precursors (ZyALD, ZrD4, TDMAHf, HfD4) and ozone. As expected, the ALD film thickness decreases with equivalent aspect ratio. However, we also observe intrinsic variation of the leakage performance, indicating increasingly non-ideal ALD behavior deeper in the trench. Physical characterization and kinetic modeling of the deposition process explains these trends, informing future process design to mitigate defects which worsen leakage at high aspect ratios.

References:
1. Paul et al., Coatings 2020, 10(1), 64.

AA-Tup-73 Atomic Layer Deposition Zinc-Doped Alumina and Alumine at Room Temperature for Flexible and Transparent Gas Permeation Barriers, Shiv Bhudia, S Wack, N Adjeroud, J Guillot, Luxembourg Institute of Science and Technology, Luxembourg; D Blondin, Met-Lux S.A.; R Leturcq, Luxembourg Institute of Science and Technology, Luxembourg
Gas permeation barriers are widely employed in many technological applications. From medium barrier properties (Oxygen transmission rate, Tuesday Afternoon Poster Sessions, June 30, 2020
Tuesday Afternoon Poster Sessions, June 30, 2020

OTR = 1 cc m⁻² day⁻¹ bar⁻¹; Water vapour transmission rate, WVTR = 1 g m⁻² day⁻¹; in the food packaging industry. To very high barrier properties (OTR = 10⁻⁶ cc m⁻² day⁻¹ bar⁻¹; WVTR = 1 g m⁻² day⁻¹) such as in flexible organic opto-electronics. Here, it is even more critical to avoid the presence of water and oxygen in the active layer.

Although, many solutions are available for high performance barriers, they typically are rigid (glass) or opaque (metal coatings) solutions, and polymeric substrates lack the capability of delivering high gas barrier properties by themselves. One promising strategy is to coat the polymeric substrate with defect free thin-films.

Atomic layer deposition (ALD) of amorphous alumina show very promising properties for passivation or encapsulation layers, in organic opto-electronics, but the deposition conditions usually require temperatures above 500 °C for highly oxidative conditions (oxygen or oxygen plasma) to obtained reasonable deposition rates and high density material. A method for producing high quality alumina below 60°C, using low oxidative conditions would be highly welcome for the highly sensitive materials used in organic electronics.

In this work, we propose a new process for low-temperature atomic layer deposition (ALD) of high-quality gas permeation barrier based on alumina on PET substrates. These can be employed in a multi stack structure of organic and inorganic thin-film layers for ultra-low gas permeation barrier for flexible and transparent polymeric substrates.

By incorporating up to 5 at. % Zn as dopant during the deposition of alumina, we demonstrate the ALD of high-quality alumina at room temperature, with ALD cycles times below 1 minute. The gas barrier properties of this new material, with oxygen and water vapour transmission rate (Mocon test), show barrier properties comparable with alumina deposited at 80°C. Furthermore, the physical diffusion mechanism of a gas through a thin-film gas barrier layer is investigated; For such purpose we developed an in-house He permeation tester.

AA-TuP-74 ALD Encapsulation of QD-Polymer Composite Films for Luminescent Applications, Natalia Zawacka, R Petitt, J Kuhls, P Smet, C Detavernier, Z Hens, Ghent University, Belgium. Because of their high photo-luminescence intensity, quantum dots (QDs) are a promising material for absorbing and converting light in photonic applications. However, they are very sensitive to the environmental conditions and their degradation presents major challenges. Many of the most promising technological applications of luminescence require thin films. Film deposition technology is well-established in the industry with a number of different techniques used for the manufacturing of both polymeric and inorganic thin films. From industrial point of view, the fabrication of QD-in-polymer composite films is extremely relevant. However, despite many potential advantages, the development of such composite films has been inhibited by the instability of the QDs when embedded into a polymer layer.

Here, we propose a two-layered thin film architecture and its fabrication method based on industry-compatible processing techniques. The strategic approach includes a combination of a QD-in-polymer composite film, overcoated with an additional oxide layer deposited via the ALD technique as an encapsulation layer. This assembly offers an increased stability, and provides a simple architecture for various luminescent thin film based applications.

An extensive study was undertaken where the degradation trends of QDs photoluminescence were assessed during the ALD process, investigating the influence of different precursors and gasses, as well as subsequent ageing tests in controlled ambient. We fabricated and tested a medium size (5x5cm²) device, using these highly scalable processes proving that it may represent a practical route to real-life applications of QD-based Luminescent Solar Concentrators.

AA-TuP-78 ALD-Grown Aluminum Oxide Coatings for Nuclear Applications, Boris Paladino, M Vanazzi, Italian Institute of Technology, Italy; S Bassini, M Ulliti, ENEA (Agenzia nazionale per le nuove tecnologie, l’energia e lo sviluppo economico sostenibile), Italy; F Di Fonzio, Italian Institute of Technology, Italy.

Nuclear energy is one of the main characters in the power production field, and it is expected to experience a great development in the next future. Among the several new designs of power plant, the fusion reactor will be a substantial turning point in the energy sector. At the time being, issues related to materials compatibility persist. According to the most relevant design, fusion reactors will take the Tritium-Deuterium fusion as the reference reaction for power generation. Thus, the availability of Tritium to fuel the reactor core assumes relevant importance. The breeding process represents one of the main focus points of technological R&D activities and the inhibition of Tritium permeation is mandatory to achieve Tritium balance in the reactor chain: once Tritium is produced, an adequate permeation barrier is required to confine it. In addition, since the breeding material is the liquid eutectic alloy Pb-16Li, corrosion issues arise from the interaction of this medium with structural steels. A viable solution to mitigate the effects of both permeation and corrosion is the deposition of a protective barrier. We report on the preliminary studies about multifunctional nanoceramic Aluminium Oxide coatings grown by Atomic Layer Deposition (ALD) technique. The samples produced were initially characterized by means of SEM, AFM and XRD. The coatings are dense, compact and uniformly covering the whole substrate. From XRD analysis it is possible to understand that the deposited material is amorphous in structure, since no sharp peaks were detected. Corrosion tests in static Pb-16Li at 550°C for 2000h showed that the coating is able to protect the steel substrate mitigating the dissolutive process of the liquid medium. Finally, permeation tests with Hydrogen are still ongoing, but the preliminary results are promising. To conclude, ALD technology represents one of the few viable solutions for materials protection for the structural steels of the breeding blanket. Deeper characterization of the coating (nanoindentation and thermal cycling) and longer corrosion tests are already planned.


Oxynitrides or nitrogen incorporated transition metal oxides are rapidly gaining attention in materials research because of their tunable electrical and optical properties. They offer usage in variety of applications like photocatalysis, phosphors, electrochemical energy storage, magnetic materials etc. Primary changes in the material properties after incorporation of nitrogen occur due to the difference in electronegativity, electronic charge and polarizability between oxygen and nitrogen atoms. However, effective and homogeneous doping in the host material is a major practical issue till date. Constructive ways to increase the conductivity without significantly altering the materials chemical properties after doping are still a challenge. Usually nitrogen incorporation is carried out by annealing oxides under NH₃ or N₂/H₂ gas environment. In such circumstances the metal ions are sensitive to reduction which results in the formation of undesirable phases in the doped materials. Also the possibility of dopant inhomogeneity is a major drawback towards obtaining good quality doped materials.

In this work we report, nitrogen-incorporated amorphous molybdenum oxide (MoO₃:N) thin films synthesized by atomic layer deposition (ALD) at relatively lower temperature of 170°C. One ALD cycle of molybdenum nitride (MoN₃) is sandwiched for nitrogen incorporation between two MoO₃ layers. The concentration of nitrogen is controlled by varying the ratio of MoO₃/MoN₃ layers. Quartz crystal microbalance (QCM) measurement is carried out to study the mass change after every single precursor dosed into the reactor. Secondary Ion Mass Spectra (SIMS) shows homogeneous distribution of nitrogen throughout the as-deposited films. Hence, uniform N-doping inclusion is adequately achieved at the reaction temperature. It is observed that conductivity of MoO₃ films increase with increase in nitrogen concentration. Room temperature and low temperature electrical properties of different films are also studied in detail to understand the transport mechanism with and without nitrogen incorporation.

Both pristine and N-incorporated MoO₃ layers are deposited on high surface area carbon nanotubes (CNTs) and applied as anode material in lithium ion batteries. As expected, addition of nitrogen helps to improve the electrochemical performance because of the increased ionic and electronic conductivity.

AA-TuP-82 Improvement of Thin-Film Transistor Performance in Atomic Layer Deposited SnO₂ Films by Thermal Annealing Process, J Lee, Su-Hwan Choi, Hanyang University, Republic of Korea; B Park, EM Index, Republic of Korea; J Sheng, J Park, Hanyang University, Republic of Korea.

SnO₂ thin films was deposited by the thermal atomic layer deposition (ALD) method using N₂-N₂-tert-butyly-1,1-dimethylethylendiamine stannylene(II) as a precursor and water as reactants. The deposited SnO₂ thin films were thermally annealed in vacuum ambient. During thermal annealing SnO₂ thin film transformed to SnO tetragonal from amorphous phase with the increase of surface roughness. Also, electrical properties (carrier concentration, resistivity) could be easily controlled by employing post...
thermal annealing treatment, SnO showed metallic to semiconductor transition as annealing temperature increased, owing to the change of the chemical bonding state existed in SnO. The combined studies of density functional theory (DFT) calculations and experimental analyses showed different density of state (DOS) depending on the defect site and chemical bonding, could explain the change of electrical properties. The fabricated ZnO thin film transistors (TFT) showed on/off current ratio of 1.27×10^4 and field effect mobility of 0.98 cm^2/Vs. The TFT bias stability were measured and SnO TFT showed good stability.

ACKNOWLEDGMENTS
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The Luxembourg Institute of Science and Technology (LIST) proposes a large atomic layer deposition (ALD) platform with complementary tools for the development of new coating processes and the improvement of existing ALD processes. The platform allows processing of various types of substrates, flat or 3D objects, flexible substrates and powders by FBR (Fluidized Bed Reactor) with up-scaling capabilities. The ALD platform is completed by other thin film deposition facilities (MOCVD, PVD), by cleanroom microfabrication capabilities to realize functional chips, and by a characterization platform (SEM-EDS, ellipsometry, contact angle, XRD, XPS, SIMS, AFM, UV-Vis-NIR spectrophotometry, Raman, photoluminescence, [IV], Resistivity) for quality control of the deposited thin films. This abstract is aiming to present ALD activities of our platform covering the requests and specifications from Fundamental Research partners on breakthrough materials to the development and small production processing for industrial partners. A selection of ALD developments will be presented in the framework of LIST research and development projects, addressing MEMS (Microelectromechanical Systems), and sensors (Figure 1). Energy Harvesters (Figure 2), Multilayers (Transparent Conducting Oxides and Al2O3) for transparent electronics (Figure 3), Example of Ag nano wires covered with conformal ALD ZnO film (Figure 4) and fillers’ coating for composites (5).

By the means of thermal ALD and Plasma-Enhanced ALD (PEALD), we developed a library of different thin films and multilayers processes including oxides (ZnO, TiO2, Al2O3, SiO2, MgO), nitride (AlN, TiN), metals (Ag, Co, Ni) aiming both fundamental Research and applicative systems.

AA-TuP-89 Atomic Layer Deposited Films for Solar Cells Application, Karol Frohlich, CEMEA/Institute of Electrical Engineering, SAS, Slovakia; M Mikolášek, Institute of Electronics and Photonics, SUT, Slovakia; R Subair, V Nadáždy, Institute of Physics, SAS, Slovakia; A Rosová, E Dobroczka, M Precner, Institute of Electrical Engineering, SAS, Slovakia; M Jergel, E Majková, Institute of Physics, SAS, Slovakia

Atomic layer deposition (ALD) is exceptional deposition technique because it allows for growth of high quality films on large substrates at low deposition temperatures. In our contribution ALD was employed for preparation of ZnO-based transparent conducting electrodes and for encapsulation of fabricated solar cells using Al2O3.

Al-doped ZnO films were used for transparent conducting electrodes. Deposition was carried out at temperatures between 150 and 250 °C on Si or quartz substrates. Diethyl zinc and trimethyl aluminium were used as precursors and water vapours as reactant. Al-doping was performed by inserting Al2O3 cycles in ZnO growth. Deposition of 1 Al2O3 layer per 7 deposition ZnO layers gave the best resistivity results. Resistivity of the Al-doped ZnO films depended on the deposition temperature and film thickness. Transition electron microscopy revealed typical columnar growth of the films with fine grained polycrystalline region close to the substrate. The films prepared at 250 °C exhibited 002 texture and for the thickness above 100 nm showed resistivity of 1 mΩcm. This corresponds to the sheet resistance of 40 Ω/square. Hall measurement revealed electron concentration of 4×10¹⁸ cm⁻³ and mobility in the range of 10-20 cm²/Vs. Optical transmittance of the films was higher than 80% in the wavelength range between 400 and 900 nm for the thickness up to 350 nm.

Inorganic-organic hybrid perovskite solar cells suffer from poor stability in ambient atmosphere. Oxygen and moisture are believed to be reason for the solar cell degradation. To protect the cells against ambient atmosphere influence ALD prepared Al2O3 films were employed for encapsulation. Trimethyl aluminum was used as a precursor while water vapours were applied as reactant. Deposition of the Al2O3 films took place at 50°C.

Power conversion efficiency of the solar cell encapsulated by 25 nm Al2O3 thin film deposited using water vapours as reactant decreased to 87% while unprotected solar cell degraded below 50% of its initial value after 40 days in ambient atmosphere. Potential cause of the perovskite solar cell degradation and its link to the basic solar cell characteristics is discussed.

This study was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 3130210T01 supported by Research & Innovation Operational Programme funded by the ERDF.

AA-TuP-95 Biocompatibility of ALD Coatings on Nano- and Microstructures: Cell Viability Studies of Murine and Human Induced Stem Cell-Derived Neurons, Robert Zierold, J Harberts, C Fendler, M Siegmund, M Schnelle, R Blick, Universität Hamburg, Germany

Micro- and nanostructured substrates form a powerful tool for building next-generation medical devices. Especially, controlled interaction of neuronal cells—a building block of the central nerve system—with the substrate allow for sensing, stimulation, gene transfection and drug delivery paving the way for developing novel conceptual devices such as integrated solar cell nanowires for retina implants, artificial bio-computing circuits, and model systems for neurodegenerative diseases, to name a few.

One key prerequisite is the long-term biocompatibility of the surface to allow for fully functional neuronal outgrowth and cell viability. However, functional nano- and microstructured devices are often based on semiconductors or polymers which contain toxic materials. During cell culturing, cellular uptake of harmful components potentially influences the stem cell differentiation process, the neuronal outgrowth or the electrophysiological properties, and can ultimately induce the cell death.

Atomic Layer Deposition (ALD) is ideally suited to conformally coat micro- and nanostructures. Often ALD of standard oxides, such as silica, titania, and alumina, are claimed to be biocompatible; however, data reporting on cell viability are mostly missing in these studies.

Herein, we present cell viability studies on different micro- and nanostructured substrates coated by ALD with standard oxides of varying thicknesses and subsequently used for neuronal cell cultivation. The determined cell viabilities are compared to plain Petri dish control substrates and well established biocompatible parylene C coatings by chemical vapor deposition.

In detail, we investigate ALD-coated 3D-printed cavity structures and freestanding nanowire arrays for outgrowth of murine and human induced stem cell-derived neurons. We show that cell viability—utilizing a viability assay with subsequent confocal microscopy—and full electrophysiological integrity—investigated by patch-clamping of individual cells—is maintained on the micro- and nanostructures.

Our results suggest that biocompatible thin film coatings can be in fact achieved by ALD. This property in combination with the ability of conformal coating renders ALD to an economically feasible key technique for application in micro- and nanostructured lab-on-a-chip devices interfaced with human cells.

Harberts et al., RSC Advances 9 (2019), 11194

Fendler et al., Advanced Biosystems 3 (2019), 1800329

AA-TuP-96 Low-Temperature PEALD of Ga2O3 Using TMGa and O2 Plasma, Ali Mohmoodinezhad, C Janowitz, BTU Cottbus-Senftenberg, Germany; F Naumann, P Plate, H Gargouri, SENTECH Instruments GmbH, Germany; K Henkel, J Plege, BTU Cottbus-Senftenberg, Germany

Gallium oxide (Ga2O3), a transparent semiconductor oxide, is promising for a wide range of applications in the fields of electronics, optoelectronics, and sensors [1]. For specific applications, low deposition temperatures are required to maintain the individual material properties of subjacent layers realized in prior process steps. The use of plasma-enhanced atomic layer deposition (PEALD) on the one hand and of a gallium precursor exhibiting a high vapor pressure on the other hand facilitates the deposition at lower substrate temperatures.

Hence, in this work thin Ga2O3 layers were deposited by PEALD with alternating pulses of trimethylgallium (TMGa) as gallium precursor and oxygen (O2) plasma at substrate temperatures in the range of 80 to 200 °C. The layers were prepared on silicon wafers in the SENTECH SI PEALD system [2] and subsequently characterized by spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), and electrical measurements.
In the SE measurements a linear thickness evolution with a growth rate of ~0.56 Å per cycle and an inhomogeneity of ≤ 2% across 4” wafers were found for all samples. While the refractive index of the Ga2O3 thin films is independent of temperature (1.86 ± 0.01 at 632.8 nm), the bandgap slightly decreases from 80°C to 200 °C (4.68 eV to 4.57 eV). Correspondingly, the permittivity of the layers determined from capacitance-voltage (C-V) measurements is constant with temperature (9.7 ± 0.2 at 10 kHz). Moreover, fixed and mobile oxide charge densities in the order of 1 to 4 × 10^{12} were derived from C-V data. In addition, the films show electrical breakdown fields in the range of 2.2 to 2.7 MV/cm. The analysis of the chemical composition of the films by XPS revealed ideal stoichiometric gallium to oxygen ratios of 2:3 accompanied by a lowest carbon contribution of ~10% for the sample prepared at 150 °C. [3]

Furthermore, these results will be complemented by a depth profiling analysis of the layer composition based on cyclic Ar+ ion sputtering using XPS.

The excellent materials properties are maintained even at low substrate temperatures as low as 80 °C confirming that the TMGa/O2:PEALD process is indeed suitable for low-temperature growth.


**AA-TuP-97 ALD Coatings on Ni-Rich NMC Cathode Materials for Long Lasting, High Energy Density Batteries, Jaime Dumont, D Lewis, M Martinez, M Herbert-Walters, S Moulton, B Hughes, A Dameron, Forge Nano

LiNi0.8Mn0.2O2, Li(Ni0.8Mn0.2)O2, and Ni(Ni0.8Mn0.2)O2 (NMC) layered oxides have been a leading material in Li-ion battery technology. By steadily increasing the nickel content in each generation, NMC materials have achieved impressive energy densities (~ 800 Wh kg⁻¹) and specific capacities (~200 mAh g⁻¹) without needing to rely on complex and impractical battery chemistries. These benefits, however, come at a cost. Increasing nickel content leads to increasing structural instabilities and severe capacity fade. Extensive research on both layered-structure oxides has revealed that many battery degradation mechanisms such as phase transformations, transition metal dissolution and particle cracking initiate at particle surfaces.1, 2

In this talk, we will explore how cathode coatings by atomic layer deposition (ALD) can preserve and stabilize Ni-rich NMC surfaces, enabling increased capacity retention and high voltage utilization. Coin cell durability studies at 0.5C/1C reveal that ALD coatings can increase cycle life by up to 400% at high voltage (4.6 V). At faster C rates (4C/1C), ALD cathode coatings showed decreased internal resistance growth and decreased absolute internal resistance over the lifetime of the cell. We elaborate on these findings using results from neutron diffraction (ND), X-ray spectroscopy (XPS) and electron energy loss spectroscopy (EELS) to fully examine the mechanism by which ALD surface coatings prevent detrimental surface reactions and lengthen battery cycle life.

References:

**AA-TuP-98 Lifetime, Selectivity, Stability, and Hydrothermal Improvements with ALD Overcoating for Hydrogenation and Dehydrogenation Catalysts, Staci Moulton, A Dameron, T Procacci, R Tracy, Forge Nano

While ALD has grown to be an essential and widely implemented technique in two-dimensional nanoscale device manufacturing, the innovative commercial development of applications for three-dimensional and porous materials have comparatively lagged. At Forge Nano, we recognize the criticality of enabling these ALD-assisted technologies for commercial applications, particularly in catalysis. We will demonstrate that ALD- overcoated catalysts, adding a metal-oxide top layer to a traditionally fabricated catalyst, enabled metal catalysts through targeted coating strategies for specific catalytic deactivation challenges. Our overcoat catalysts retain activity, physical stability in hydrothermal and thermal conditions, achieve improvements in selectivity, and significantly enhance lifetime. For hydrogenation of muconic acid to adipic acid, the Al2O3 ALD-coated catalysts retain up to two-fold activity for Pd on TiO2 support. Second, the Pd leaching from the catalyst was reduced by four-fold on the ALD-coated catalyst. The same Pd on TiO2 catalyst with ALD-overcoat showed significant resistance to physical restructuring under thermal treatment conditions shown both by STEM-EDS elemental mapping and activity data for uncoated and ALD-overcoated catalysts. Thermal treatment, or catalyst regeneration cycles, reduced the active catalyst surface area by over 80% for the uncoated catalyst while the ALD-overcoated catalyst retained all its active surface area over 5 regeneration cycles. The benefits of ALD for catalysis are proving to be a fertile working ground for both active materials and overcoat applications.

**AA-TuP-100 Efficient and Flexible Dielectrics at Elevated Temperatures from Polymers Sandwiched with Wide Bandgap Inorganic Films Grown via Atomic Layer Deposition, A Okyay, Stanford University; S Ilham, C Wu, A Mohammad, D Shukko, Y Cao, Necmi Biyikli, University of Connecticut

Flexible dielectrics with ultra-high power density are core components of electronic and electrical applications in terms of energy storage, power converter, electrical insulating, etc. However, the drastically increased conduction current at high electric fields and elevated temperatures limited their development in applications under harsh conditions (e.g., aerospace and downhole fossil energy exploration) or systems with cutting-edge wide bandgap semiconductors, where the temperature could reach or surpass 150 °C. Reported here are flexible dielectrics based on Kapton® polyimide (PI) sandwiched with wide bandgap inorganics coated via thermal and plasma-assisted ALD, revealing greatly suppressed conduction current. Thin films of Al2O3 and Ga2O3 were separately grown on Kapton® using thermal and plasma-assisted atomic layer deposition (PA-ALD), respectively. Metal precursor and oxygen co-reactant for the process included hexamethylditin (HMDS) with TMGa and triethylaluminium (TEA) with TEG. The ALD growth was performed at 200 °C substrate temperature. The charging-discharging efficiency investigated by high electric field displacement-electric field (DE) loops was significantly improved, particularly under high electric fields and elevated temperatures. Films of varying thicknesses: 50 - 160 nm Al2O3 and 30 - 50 nm Ga2O3 were grown to study the charging-discharging efficiency. For the Al2O3 coating, the efficiency increased with 50 nm film when compared to 160 nm. However, the highest efficiency improvement was obtained for the plasma-assisted ALD grown Ga2O3 film, which possibly resulted in better blocking the charge injection in the film and thus good control of the conduction losses. Further tests were performed to study the effect of thinner and plasma-enhanced ALD grown Al2O3 on the charging-discharging efficiency enhancement of Kapton® flexible dielectrics. ALD as a facile and scalable fabrication technique would enable enormous potential in large scales of roll-to-roll processing for industrial high-power electrical cabling applications.

**AA-TuP-101 On the Atomic Layer Deposition of Catalysts for Dehydrogenation of Propane with CO2: The Study of Reaction Performance and Coke Formation, Fatemeh Gashoul Daresibi, Y Mortazavi, A Khodadadi, University of Tehran, Iran

Increasing the worldwide demand for propylene, inspired researchers for the study of promoted highly advanced techniques compared to the current industrial methods to fulfill the requirements of the market. Regarding this issue, CO2-ODHDP has attracted attentions due to its role in facilitation of the C-H bond activation, lowering the activation energy of the reaction as a whole and more effectively reduce the process temperature with much higher rates without the problem of deep oxidation or low selectivity.

In this study, we applied the atomic layer deposition of CrO2/SiO2 to enhance the performance of CO2-ODHDP reaction. Silica supported chromium oxide catalyst was synthesized by using Cr(acac)3 and synthetic air as metal precursor and oxidant respectively. The support temperature was selected in the suitable range of ALD called ALD-window and the precursor dose time was 9 h. The outlet of the ALD reactor was monitored by an on-line FTIR gas cell. The loading of Cr was determined by ICP-oes.

The ALD catalyst was used for the dehydrogenation of propane in presence and absence of CO2. The oxidation step followed by stabilization of catalysts was carried out at three different temperatures, 300, 600 and 650°C. Results reveal the higher performance of ALD catalyst in presence of CO2 compared to direct dehydrogenation. However, in both conditions, catalyst suffers from deactivation through the time-on-stream possibly due to the structural changes during the reaction, irreversible reduction of Cr⁴⁺ and coke formation. The catalyst with lower oxidation and stabilization temperature, 300°C, has shown the higher reaction performance close to equilibrium conversion. The coke formation was studied with Raman spectroscopy and Temperature Programmed Oxidation (TPO) accompanied by on-line FTIR analysis. Results illustrate the presence of both graphic
and disordered carbonaceous species. The main product of the coke combustion was CO₂ with a very slight amount of CO. To find out the coke source, Ar diluted propylene was passed through the catalyst and the Raman results show a similar spectrum revealing the propylene as the main source. The adsorption-desorption isotherm and pore size distribution curves show slight structural changes after reaction. Temperature programmed reduction (TPR) over fresh and regenerated spent catalyst also shows a little decrement in reducibility of catalyst as another sign of structural changes and/or irreversible reduction of chromium (VI). To summarize, the ALD-synthesized Cr/SiO₂ catalysts show higher performance at lower oxidation temperature and in presence of CO₂ while the deactivation under reaction conditions is still an issue.

AA-TuP-103 Atomic Layer Deposited Al-doped TiO₂ as Passivating Contacts on Silicon Solar Cells, Borong Song, University of New South Wales, Australia; Z Huang, Jiangsu Ocean University, China; M Hossain, University of New South Wales, Australia; A Abdallah, Y Zakaria, QERI, Qatar; B Hoex, University of New South Wales, Australia
Atomic layer deposited (ALD) titanium dioxide (TiO₂) has been well investigated and has been reported to be an excellent electron selective contact on silicon solar cells with a high level of surface passivation; however, its poor thermal stability[1][2] limits the range of processes which can be used after the application of the TiO₂ film which is, in particular, a significant restriction for the metallization step. Aluminum (Al) doped TiO₂ is reported to effectively improve perovskite solar cell performance especially in electric properties via creating defects due to the size discrepancy between Ti and Al atoms [3]; however, ALD doping materials are yet to be thoroughly investigated applying on silicon solar cells as passivating contacts.

In this work, Al was successfully incorporated into TiO₂ layers using an ALD supercycle approach at 150 °C, showing both passivation and electrical performance of superior quality on silicon wafers. A champion effective minority carrier lifetime of 1.9 ms is obtained from Al-TiO₂/SiO₂/n-Si stack after 300 °C annealing while a significantly lower lifetime of 210 µs is obtained from the undoped reference. This indicates that Al incorporation increases the thermal stability of the TiO₂ layer and the passivation effects, and this is very beneficial from an application point of view. TLM measurement showed that contact resistance also reduces by introducing Al into the TiO₂ layer, which can probably be attributed to the defect states introduced by Al. Furthermore, DFT simulation results well explained the mechanisms of improved performances from experimental results. Future work will focus on fabricating solar cell devices employing this doped layer as electron selective contact to further improve the solar cell efficiency.

References

AA-TuP-105 The Evolution of Temperature Monitoring in ALD, J Paolino, Jason Merson, Global Results Communications
The advancement and complexities in semiconductors are the foundation for continued technology advancements in virtually every device and machine we interact with. As semi structures become more complex, processes like Atomic Layer Deposition (ALD) are exceedingly important to ensure deposits are precise and can interconnect with the different layers. Even though these processes have been out there for people to explore, ALD has been too expensive to pursue. But now, advancements are making ALD economically feasible and the market is expected to rapidly expand within the next few years.

As ALD becomes a highly utilized deposition method, the industry should expect to see more complex structures where the measurement of temperature becomes increasingly important as a control variable. Traditionally with ALD, thermocouples have been used to monitor temperature, but these only provide an indirect measurement that requires a model to calculate the offset. This becomes problematic over time because as the thermocouple degrades the model changes making temperature readings harder to determine and unreliable. Now we are seeing a push for a better solution for measuring temperature with precision as more semiconductor manufacturers adopt ALD.

During this presentation, Advanced Energy – a global leader in highly engineered, precision power conversion, measurement and control solutions – will discuss how the industry is now moving towards the adoption of optical temperature measurement tools, such as non-contact pyrometers that can get within 2mm of a silicon wafer without causing damage or interrupting the ALD process. This will include:

• A look at the evolution of temperature reading in ALD and its challenges
• How pyrometers provide precise, non-contact temperature readings

The importance of emissivity measurement
Gallium nitride (GaN) is a key material in high electron mobility transistors (HEMT) based on the group 13-nitrides. These structures are routinely made by CVD at high temperatures (1000 °C) using trimethylgallium (TMG) and NH₃. These high deposition temperatures hinder the exploration of GaN films on temperature sensitive materials such as InN, which is highly desirable to integrate into HEMTs due to its high electron mobility. ALD is a low temperature alternative that could be used to deposit high quality GaN. GaN has previously been explored by ALD using trimethylgallium (TMG) or triethylgallium (TEG) together with N₂/H₂ plasma [1], NH₃ plasma [1] and thermal NH₃. However, these GaN films were found to be non-stochiometric and show high amounts of C and O impurities, which is undesirable in materials to be used in electronics.

Herein, we report on two alternative Ga precursors: tris(dimethylamido)gallium(III) ₁ and tris(1,3-disopropyltriazenide)gallium(III) ₂ and their use in ALD in combination with NH₃ plasma to deposit GaN. These two precursors possess Ga–N bonds instead of Ga–C bonds like TMG and TEG. As the Ga–C bond is stronger than the Ga–N due to its more covalent nature of the bond, precursors with Ga–N bonds could potentially have a more favourable surface chemistry with lower impurity levels. Both ₁ and ₂ show self-limiting deposition behaviour for GaN growth. Precursor ₁ saturates after 4s and 6s of NH₃ plasma exposure, with 10s purge between to give a growth rate of 1.4 Å/cycle. The growth remains constant at 1.4 Å/cycle between 130-250 °C. GaN growth from ₂ shows a growth rate of 0.3 Å/cycle which is constant between 300-350 °C.

GaN deposition directly 4H-SiC (0001) using these ALD processes grew with the epitaxial relationships of GaN(0002)∥SiC (0002) and GaN (10-13)∥SiC (10-12). This set these ALD processes apart from traditional MOCVD of GaN as the later requires an AlN buffer layer for epitaxial growth of GaN on SiC.

The composition of the films was measured with RBS/ERDA. Precursor ₁ gave GaN films with 45.7 at.% Ga, 47.2 at.% N, 3.1 at.% O, 2.8 at.% C, 1.2 at.% H, giving a Ga/N = 0.97. GaN grown from ₂ has 48.8 at.% Ga and 46.4 at.% N giving a Ga/N = 1.05. GaN from ₂ contained 3 at.% O, 1.8 at.% H and no detectable carbon. Absorption measurements show the optical bandgap of the GaN to be 3.42 eV, which is close to the theatrical value of 3.4 eV. Fermi level measurements with XPS show that the fermi level is closer to the conduction band then the valence band, making the GaN film unintentionally n-type doped.

In GaN power device, gate dielectric is required that they have more stable amorphous structure at 800 °C, relatively high dielectric constant (k) value (>10) and high breakdown electric field (>8 MV/cm). For these reasons, we have been investigated Hf-rich HSIGO, as gate dielectric [1, 2]. To fabricate HSIGO films, the HfO2/HSIGO laminate was initially deposited by PE-ALD with tetrakis(dimethylamino)hafnium (TDMAHf) and Tris(dimethylamino)lsilane (TDMAS) precursors [1]. Understanding the SiO2 growth mechanism on HfO2 layer is an important in terms of the design of the HSIGO formation. The growth per cycle (GPC) values of PE-ALD-SiO2 layer on HfO2 underlayer was 4 times larger than that on SiO2 underlayer because of the different adsorption of TDMAS precursor on the surface of SiO and Hf-O which has the difference of electronegativity. Using the GPC of PE-ALD-SiO2 layer on HfO2 underlayer, we could design Hf-rich HSIGO (Hf5Si5Ox) films by controlling ALD cycle of each HfO2 and SiO2 layer. The Hf5Si5Ox dielectric of n-GaN capacitors exhibited superior characteristics such as an amorphous structure after annealing at 800°C, high k value of 13.5, a small flatband voltage shift (−0.36 V), a high breakdown electric field (8.6 MV/cm).

In our previous work, we achieved a low thermal budget process (400 °C) under large tensile strain (about 3.5 GPa) using TiN top and bottom electrodes. The HfO2 films using the TiN electrodes can prevent degradation of the ferroelectric properties from hydrogen incorporation owing to the TiN electrodes can act as a barrier layer against hydrogen diffusion. However, during the deposition of HfO2 film using atomic layer deposition (ALD), the choice of oxygen source can affect the residue in the deposited film. When hydrogen-related substances are used as the oxygen source, the ferroelectric properties can be altered by the residues remaining in the HZO film. Therefore, in this study, we investigated the effects of the oxygen source, especially O2, H2O, and Deuterium oxide (D2O) on the ferroelectric properties of the ALD-HZO films. The HZO films with Hf:Zr ratio of 1:1 were deposited on the TiN bottom electrode by ALD using TDMAD-Hf and TDMAD-Zr as the precursors of Hf and Zr, while O2, H2O, or D2O as the oxidant. After the TiN top electrode was deposited, rapid thermal annealing was done, and metal-insulator-metal capacitors were fabricated using a Pd/Au hard mask and wet etch process.

Regardless of the oxidant, the HZO films exhibited the formation of a non-centrosymmetric orthorhombic phase which is origin of the ferroelectricity. However, it was confirmed that the ferroelectricity of the HZO film deposited with the source related to hydrogen such as H2O and D2O, is worse than the HZO film deposited with O2. From the polarization-electric field curves, the remnant polarization (P r) of O2-, H2O-, and D2O-based HZO devices was 47, 38, and 34 μC/cm2, respectively. Whereas, the H2O- and D2O-based HZO devices exhibited higher leakage current than that of O2-based device. We suspected that the degradation of P r and the leakage property is caused by more hydrogen incorporation in the HZO film when H2O and D2O oxidants are used. The result implies that the use of O2 as the oxygen source is advantageous for improving ferroelectric properties of the ALD-HZO films.

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1:45pm AA-WeA-4 Deposition of Inherently Ferroelectric Films by ALD Using ZrO-4 and HfO-4, Vijay K. Narasimhan, Intermolecular, Inc.; J Lehn, EMD Performance Materials; K Uttam, Intermolecular; J Woodruff, R Kanjola, EMD Performance Materials

ALD HfO2- and ZrO2-based ferroelectrics enable novel, CMOS-compatible devices for both logic and memory. Although the most stable bulk crystal structure of these materials is a monoclinic phase, this phase does not support ferroelectricity. Other polymorphs (for example, some orthorhombic and rhombohedral phases) have the symmetry required to support ferroelectric switching behavior, while still others (for example, a tetragonal phase) can be anti-ferroelectric. In many hafnium oxide and zirconium oxide ALD processes, the thin films are amorphous as deposited. Therefore, obtaining a desired ferroelectric phase depends not only on the deposition conditions of the film itself, but also on the choice of capping interfaces and annealing conditions after deposition.

Here, we demonstrate a pathway to achieving phase control in zirconia and hafnia ALD films that does not depend on capping or post-deposition annealing. We use the advanced metallocene precursors (MeCp)2Zr(OMe)Me and (MeCp)Hf(OMe)Me (commonly known as ZrO-4 and HfO-4, respectively). These precursors have an ALD window that can extend to near or above the crystallization temperature of zirconia and hafnia thin films. Using GI-XRD, we examine the phase of films deposited with different reactants (i.e. water and oxygen), growth temperatures, and thicknesses. We show that, for ZrO in particular, the as-deposited films are crystalline across a wide process space and that the films are phase-stable after subsequent thermal processing. We extend previously published results to elucidate a processing window where the non-ferroelectric monoclinic phase can be substantially suppressed. We use the results from the unit film studies of ZrO2 and HfO2 to create a blended ZrO2/HfO2 film that is inherently ferroelectric, demonstrating strong remanent polarization with no explicit post-deposition cap and annealing. These results provide a pathway to developing ferroelectric devices in which the electrodes and thermal processing conditions of the entire stack can be optimized independently with minimal effects on the ferroelectric layer.

2:00pm AA-WeA-5 Ferroelectricity of 300°C Low Temperature Fabricated Hf,Zr,Ti-O Thin Films by Plasma-Enhanced Atomic Layer Deposition using Hf/Zr Cocktail Precursor, Takashi Onoaya, Meiji University, Japan; T Naboratene, National Institute for Materials Science, Japan; Y Jung, University of Texas at Dallas; H Hernandez-Ariaga, The University of Texas at Dallas; J Mohan, University of Texas at Dallas; H Kim, A Khosravi, The University of Texas at Dallas; N Sawamoto, Meiji University, Japan; C Nam, E Tsai, Brookhaven National Laboratory; T Nagata, National Institute for Materials Science, Japan; R Wallace, The University of Texas at Dallas; J Kim, University of Texas at Dallas; A Ogunra, Meiji University, Japan

Recently, low temperature fabrication process for ferroelectric Hf,Zr,Ti-O (HZO) films has attracted a lot of attention for use in future device applications, such as FeRAM and FeFET. The amorphous HfO2 films deposited by thermal atomic layer deposition (TH-ALD) using H2O or O2 as an oxidant gas were generally employed, then, an annealing process at >400°C with TiN top- and bottom-electrodes (TE- and BE-TiN) was performed to obtain ferroelectric orthorhombic (O) phase due to inducing tensile stress from TiN to the HZO film. [1] On the other hand, we focused on plasma-enhanced ALD (PE-ALD) using O2 plasma, because the as-grown HZO film had nanocrystalline structure with O, tetragonal, and cubic (O/T/C) phases. In this work, we studied the ferroelectricity and crystallinity of PE-ALD HZO films using a low temperature annealing process at 300–400°C.

The TiN/HZO/TiN capacitors were fabricated as follows: A 10-nm-thick HZO film was deposited on BE-TiN by PE-ALD at 300°C using (Hf/Ze/Ti)[(C,H2O)2H2O ] (Hf/Ze/Ti = 1:1) cocktail precursor and O2 plasma. TE-TiN was then fabricated by DC sputtering. Finally, post-metallization annealing (PMA) was performed at 300–400°C for 1 min in a N2 atmosphere. Pulse write/read measurement was employed to obtain the remanent polarization (P_r) and dielectric constant (κ). [1] The crystallinity was analyzed using synchrotron wide-angle X-ray scattering (WAXS) at NSLS-II, Brookhaven National Laboratory.

The PE-ALD HZO film after PMA at 300°C clearly showed ferroelectricity with P_r of 28 µC/cm² and exhibited high k of 41, while the HfO2-based films with stable ferroelectricity using a lower process temperature below 400°C have not been reported. The P_r of PE-ALD HZO films increased with PMA temperature. For synchrotron WAXS patterns of PE-ALD HZO films, the peaks originating from O/T/C phases were clearly observed while those from the paraelectric monoclinic (M) phase were suppressed using a low temperature PMA process even at 300°C, leading to the stable ferroelectricity. This might be because nanocrystal grains with O/T/C phases in the as-grown HZO film play an important role as nuclei for the crystal growth of the HZO film during PMA process, while the as-grown HZO film deposited using TH-ALD typically have an amorphous structure. In addition, the phase transformation from C-phase to O/T-phases was observed as PMA temperature increased, resulted in high P_r.

In conclusion, PE-ALD and a low temperature PMA process at 300°C are promising methods for the fabrication of ferroelectric HZO films with superior P_r.

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2:15pm AA-WeA-6 Atomic Layer Deposition of GeS Film for 3D Cross-Point Memory Scaling, Myoungsub Kim, Y Kim, I Sohn, H Kim, Yonsei University, Republic of Korea

Recently, the emergence of storage class memory (SCM) in the memory hierarchy has attracted attention as a new role for improving the performance of computing systems [1]. The 3D cross-point (X-point) memory using chalcogenide amorphous materials as ovonic threshold switching (OTS) selectors, is the most powerful product for SCM and already requires future scaling research. The X-point memory of today’s planar 3D structure is expected to change to a vertical 3D X-point structure, as in the history of NAND flash, so it is necessary to study chalcogenide ALD for OTS application.

We present ALD study of GeS thin film motivated by the expectation of lower off-current for device scaling and larger array implementations because it is known to have higher optical bandgap than GeTe and GeSe films, recently published in ALD studies [2][3]. The ALD GeS amorphous film synthesis using commercially available GeCl4 precursor and H2S reactant was minutely investigated on RF plasma, temperature effect and interesting non-conventional saturation growth behavior. GeS films were identified quantitative composition and impurities level through auger electron spectroscopy (AES) depth profile analysis, and the tunable Ge and S composition ratio results were obtained by controlling the deposition temperature and plasma power. And excellent thermal stability of GeS amorphous film up to 600°C was confirmed using in situ heating X-ray diffraction (XRD). In addition, atomic layer deposited GeS film was confirmed the good conformity in the vertical 3D patterned wafer using focused ion beam transmission electron microscopy (FIB-TEM).

Finally, the devices fabricated using ALD GeS were studied the scaling effect of OTS electrical characteristics on the decrease of GeS film thickness from 30nm to 5nm and the decrease of bottom electrode contact size from 80nm to 40nm. The achievement of a novel binary GeS ALD study for OTS selector will contribute to the development of 3D X-point memory scaling in the future.


3:00pm AA-WeA-9 Atomic Layer Annealing of AlN to Template The Growth of High Thermal Conductivity Heat Spreader Films, S Ueda, A McLeod, University of California, San Diego; M. Chen, C Perez, E Pop, Stanford University; D Alvarez, RASIRC; Andrew Kummel, University of California, San Diego

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The low-temperature (<400°C) deposition of polycrystalline AlN films is demonstrated by atomic layer annealing (ALA) which is a variant of ALD that utilizes a third pulse of ions in addition to the usual metal and co-reactant pulses [1]. As transistor size continues to decrease, it becomes a significant challenge to remove the heat generated during the operation of microelectronic circuits. The use of electrically conductive heat spreaders complicates 3D integration in VLSI CMOS or stack memory devices and induces parasitic losses in RF MMICs. Crystalline AlN has a thermal conductivity close to that of Cu and is a good electrical insulator making it an ideal heat spreader material.

Using trimethyl aluminum (TMA) and the highly reactive nitrogen-containing precursor hydrazine (N2H4), AlN can be deposited at 200°C [2]; however, these films are amorphous and would have low thermal conductivity due to phonon scattering. Using tris(dimethylamido) aluminum (TDMAA) or tris(diethylamido) aluminum (TDEAA) with N2H4 or NH3 at temperatures >350°C, polycrystalline films can be deposited in a purely thermal process; however, the reported grain sizes are small (<5 nm) or there is a mixture of polycrystalline and amorphous phases [3-4]. ALA has been used to deposit crystalline films such as AlN [5] and GaN [6] at low temperature, but a nitrogen-containing plasma was used. In the present study of AlN ALA, two metal precursors (TMA and TDMAA) were compared using anhydrous N2H4 as a co-reactant and argon ions with tuned energy for the third pulse. High-quality AlN films are deposited with large grain size and low C/O contamination which can then be used as a templating layer for further high-speed AlN film growth.

The deposition of high quality, stress controlled AlN films deposited by ALA are successfully used as templates for thicker heat spreading layers deposited via sputtering and polycrystalline sputtered AlN films with near-record thermal conductivities of ~70 W/mK were obtained for sub-0.5 micron thick films.


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Thin film MIM tunnel diodes are finding increasing interest for high-speed applications such as THz detection and energy harvesting. Asymmetry of current density vs. field (J-E) \(f_{\text{sym}}=1/2\) in MIM diodes is typically achieved through the metal electrode work function difference \(\Delta \phi\). Using ALD to form an asymmetric nanolaminate insulator tunnel barrier enables MIM diodes that exhibit enhanced low voltage performance due to “step tunneling” in which electrons under one polarity tunnel through only the wider gap insulator instead of both.\(^1\) Replacing the narrow Ep insulator with one containing intrinsic defects, further improves low E performance via “defect-enhanced direct tunneling” (Fig. 1).\(^2\)\(^3\) Here, we investigate the impact of intentionally introduced extrinsic defects by using ALD to place Ni at precise locations in an ALD Al₂O₃ MIM tunnel barrier.

ALD of Al₂O₃ on TiN bottom electrodes was performed at 200 °C using TMA and H₂O. Five samples were prepared in which a baseline 100 ALD cycle Al₂O₃ sequence (10 nm thick) was interrupted by two ALD cycles of Ni\(_{40}^3\text{DAD}\) and O\(_6\), after either 25, 50, 75, or every 25 cycles of Al₂O₃ (Fig. 1). Al was then evaporated through a shadow mask. As-deposited MIM devices were tested with bias applied to the Al top electrode.

DC J-E sweeps of the 100 ALD cycle Al₂O₃-only device show Fowler-Nordheim tunneling (FNT) at high E, with \(f_{\text{sym}}>1\) due to \(\Delta \phi=0.2 \text{ eV}\) (Fig. 2). The addition of Ni cycles in all cases leads to an increase in J at low E, suggesting defect-related conduction. At high E, however, J of all Ni containing devices is lower than the baseline 100 c device, suggesting suppression of FNT. The 25/2/75 and 75/2/25 (Al₂O₃/NiO/Al₂O₃) devices show reversed polarity asymmetry to the 100 c device, while the symmetrically doped 50/2/50 and 25/2/25x3 devices are roughly symmetric. The reduction in J at large negative E, \(f_{\text{sym}}\) reversal, and reduced J-E slope for the Ni devices suggest the presence of negative charge in the Al₂O₃. Internal photoemission (IPE) spectroscopy reveals modified metal/insulator barrier heights and MIM and MOS CV sweeps (Fig. 3) show positive shifts in \(\text{V}_\text{C}_{\text{mow}}\) and \(\text{V}_\text{sh}\), respectively, for all Ni devices. Taken together, these results suggest negative charge in the Al₂O₃ associated with the ALD Ni impurities.

The asymmetry reversal demonstrates the potential of ALD for precision defect engineering of MIM tunnel devices. J-E, C-V, temp-J-V, frequency-CV, IPE, TEM crosscuts, and annealing will be presented.


Recently, two-dimensional electron gas (2DEG) has attracted great attention due to its presence at various heteroepitaxial perovskite oxide interfaces. Typically, epitaxial LaAlO\(_3\)/single-crystal SrTiO\(_3\) (LAO/STO) heterostructure shows high density of electrons (~\(10^{12}-10^{14} \text{ cm}^{-2}\)) confined at the oxide interface, where the density is about ~100 times higher than that of a typical semiconductor interface (~\(10^{11}-10^{12} \text{ cm}^{-2}\)).\(^1\) Creation of 2DEG is conventionally defined on the basis of discontinuity in polarity linked with the difference in the charge of the atomic layers. Simply, it can be described as half an electron being transferred to the interface to avoid the potential divergence, “polar catastrophe”.\(^2\) Another mechanism is associated with the generation of oxygen vacancies (V\(_o\)) at the surface of the STO layer during LAO or Al₂O₃ layer deposition, acting as electron donor for the 2DEG formation. It provides an opportunity for 2DEG realization for various oxide heterostructures and fabrication processes. Recently, we reported \(V_o\) generation mechanism-based 2DEG formation process using atomic-layer-deposited (ALD) ultrathin (~10 nm) binary metal oxide heterostructure. 2DEG layer can be formed at the interface of Al₂O₃/STO heterostructure on a thermally oxidized SiO\(_2\)/Si substrate at a low temperature (< 300 °C) without any epitaxial layer.\(^3\) The Al₂O₃/STO heterostructure has comparable electrical properties with typical LAO/STO epitaxial 2DEG system at room temperature (sheet carrier density, \(n_{\text{sh}}\approx 10^{13} \text{ cm}^{-2}\), electron mobility, \(\mu_\text{e} \approx 4 \text{ cm}^2/V\text{s}^{-1}\)). An in-situ resistance measurement directly demonstrated that the resistance of the oxide heterostructure interface dropped significantly with the injection of trimethylaluminum (TMA) molecules, indicating that \(V_o\) were formed on the TiO\(_2\) surface during the TMA pulse in the ALD of the Al₂O₃ film, such that they provide electron donor states to generate free electrons at the interface of the ultrathin Al₂O₃/STO heterostructure.\(^4\) In this work, we demonstrate improved field-effect transistors (FETs) using ultrathin Al₂O₃/STO heterostructure 2DEG system with a high on-current (\(I_{\text{on}} > 12 \text{ A/m}\)), low off-current (\(I_{\text{off}} < 10^{-10} \text{ A/m}\)), high on/off current ratio (\(I_{\text{on}}/I_{\text{off}} > 10^9\)), and low subthreshold swing (SS ~100 mV/dec.), which outperforms the oxide heterostructure-based FETS reported so far. Ultrathin (~7 nm) TiO\(_2\) bottom layer is easy to fully depleted, allowing an extremely low \(I_{\text{off}}\) and low SS with maintaining high \(I_{\text{on}}\) via 2DEG channel with a high carrier density at the interface. The heterostructures with the other ultrathin oxide combinations (< 5 nm) were also studied.

1:00 PM