ALD Applications
Room Van Rysselberghe - Session AA1-MoA
Emerging Applications of ALD I & II

Moderators: Hyeontag Jeon, Hanyang University, Viljami Pore, ASM

1:45pm **AA1-MoA-2 Resistive Switching Maps for Films of Variable Conductivity Grown by Atomic Layer Deposition***, **Kaupo Kukli,*** University of Tartu, Estonia*; M Kemell,* University of Helsinki, Finland*; H Castán, S Dueñas,* University of Valladolid, Spain*; M Heikkilä,* University of Helsinki, Finland*; J Kozlova, M Rähn,* University of Tartu, Estonia*; M Ritala, M Leskelä,* University of Helsinki, Finland

Multilayers of oxide thin films offer an attractive basis of resistively switching media. To effectively modify the density of useful defects, properties of wide-band-gap and high-k oxides can be tailored, e.g. in Al_2O_3-TiO_2 multilayers [1]. In addition, components with high magnetic or electric polarizability may be applied as constituents, when seeking even wider functionality of switching materials. Thereby, alternate layering of more and less insulating materials can accompany with detrimental film conductivity, lowering the ratio between low and high resistivity states.

Nanolaminates with tunable composition, such as Ta_2O_5-TiO_2 [2], ZrO_2-Co_3O_4 [2], ZrO_2-Al_2O_3 [3], SiO_2-Nb_2O_5 [4], SiO_2-Fe_2O_3 [5] were grown. In such films, electrical and magnetic polarization hystereses were monitored at room temperature, together with resistive switching behavior. The latter was destabilised in structures where leaky constituents, e.g. Nb_2O_5 and Fe_2O_3, were applied. Complementarily to the common direct current resistive switching measurements with voltage pulses, we report the application of small-signal measurements. This allows memory mapping based on two-state capacitance and conductance recorded under bipolar voltages. Such hysteron-like signal-programming voltage behavior may allow reading information especially in materials which otherwise tend to remain in low resistance state in direct current measurements.

References:

[1] P. F. Siles et al., Tuning resistive switching on single-pulse doped multilayer memristors, Nanotechnology 24 (2013) 035702.

[2] S. Dueñas et al., Memory maps: Reading RRAM devices without power consumption, ECS Transact. 85 (2018) 201.

[3] H. Castán et al., Study of the influence of the dielectric composition of Al/Ti/ZrO_2:Al_2O_3/TiN/Si/Al structures on the resistive switching behavior for memory applications, ECS Transact. 85 (2018) 143.

[4] K. Kukli et al., Resistive switching in silicon oxide-niobium oxide thin films grown by atomic layer deposition from niobium pentaethoxide and hexakis(ethylamino) disilane, Nanotechnology, In press.

[5] K. Kukli et al., Atomic layer deposition and properties of mixture films and nanolaminates consisting of iron and silicon oxides, to be published.

3:00pm **AA1-MoA-7 Understanding and Controlling Release and Aerosolization of Inhaled Drug Particles Engineered by Atomic Layer Deposition***, D La Zara, F Sun, F Zhang,* Delft University of Technology, Netherlands*; M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden*;* ***Ruud van Ommen,*** Delft University of Technology, Netherlands

Inhaled drug delivery is the administration route of choice especially for respiratory diseases such as asthma and chronic obstructive pulmonary disease. However, the rapid absorption of inhaled drugs in the lungs limits their therapeutic effect, which lasts in the case of budesonide, a common drug for respiratory diseases, a couple of hours, thus requiring multiple doses per day. Moreover, an increasing number of inhaled drugs includes amorphous and sensitive drugs, which require solid-state stabilization, as well as powders with poor flowability, which necessitate improved aerosolization efficiency to meet the drug load requirements. Therefore, to improve patient compliance and enhance the therapeutic performance, it is crucial to find novel solutions to increase the lung deposited drug as well as extend the drug release in the lung.

In this work, we deposit nanoscale Al_2O_3, TiO_2 and SiO_2 films on micronized budesonide particles to tailor their dissolution and aerosolization properties. The ALD process is carried out at nearly ambient conditions in a fluidized bed reactor for a cycle range from 10 to 50, using TMA/O_3, $TiCl_4$/H_2O and $SiCl_4$/H_2O as precursors for Al_2O_3, TiO_2 and SiO_2 ALD, respectively. Transmission electron microscopy (TEM) coupled with energy dispersive X-ray mapping reveals the deposition of uniform and conformal TiO_2 and SiO_2 nanofilms, and the occurrence of Al_2O_3 subsurface growth. In fact, due to its high reactivity, TMA penetrates into the budesonide particles forming inorganic-organic shells which consist of a Al_2O_3/budesonide mixture. In-vitro dissolution tests and cell studies reveal dramatically slowed release with increasing film thickness. In particular, the in-vitro dissolution tests correlate with the cell studies which highlights the accuracy in describing the release of inhaled drug powders. The dissolution mechanism and the role of the nanofilms during drug release are investigated by ex-situ TEM of the solutions at different time points after the dissolution test. Furthermore, in-vitro aerosolization testing by fast screening impactor shows an almost 3-fold and ~2-fold increase in fine particle fraction (FPF: % <5 µm, i.e., particle size range relevant for inhalation) for the SiO_2- and TiO_2- 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.

3:15pm **AA1-MoA-8 In-vitro Screening of Materials and Laminates by Atomic Layer Deposition for Medical Device Coatings***, R Ritasalo,* Picosun Oy, Finland*; O Ylivaara,* VTT Technical Research Centre of Finland Ltd, Finland*; T Sillanpää, P Holmlund, A Kärkkäinen,* VTT Technical Research Centre of Finland, Finland*;* ***Tom Blomberg,*** Picosun Oy, Finland

Motivation: Chronic disease monitoring and treatment is and will continue to be the most important issue related to ever-increasing healthcare costs. Chronic diseases are linked with lifestyle problems and aging population. Therefore, new technical solutions, which would decrease the direct patient care, are actively investigated. Many different coating technologies and materials are used in medical applications depending on the desired properties of the coating. Coatings are typically used for reducing friction, providing electrical insulation, and as corrosion barriers. Atomic layer deposition (ALD) coatings are known to work excellently as hermetic barriers for water vapour, however, the barrier properties in aqueous solutions mimicking the environment of the human body are still under investigations. Potentially, ALD films could work as metal ion barriers in e.g. *orthopedics* implants and as electronic insulation for implantable electronics in cardiology and neurology segments. Irrespective of the actual use, the implantable medical device must withstand the corrosive environment inside the human body for prolonged periods of time. Hermetic sealing of the device to protect it from the corrosive environment of human body and vice versa is a key step to enable long life time for the smart medical devices.

Method: The degradation of the ALD-coated Si/SiO_2/Al interdigitated electrodes (IDEs) were 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 Al_2O_3, SiO_2 and HfO_2 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 SiO_2-HfO_2 [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.

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

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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 Rodríguez, K Barton, R Peterson,* ***Neil Dasgupta,*** 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 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 (μ_{FE}). 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 μ_{FE} values of > 13 $cm^2V^{-1}s^{-1}$ 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 µm resolution, well below the resolution of traditional ink-jet printing. Finally, printed TFTs were fabricated, demonstrating well-behaved device performance, including an on/off current ratio of almost 10^6. 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. J. Sheng et al. *J. Vac. Sci. Technol. A* **36**, 060801 (2018)

2. P. Schlupp et al. *Adv. Electron. Mater.***1**, 1400023 (2015)

3. J.-U. Park et al., *Nature Materials* **6**, 782 (2007)

4:15pm **AA1-MoA-12 Optimized Schottky Junctions by Atomic Layer Deposition for Piezotronic MEMS Strain Microsensors***, **Raoul Joly**, S Girod, N Adjeroud, M El Hachemi, P Grysan, T Nguyen, K Menguelti, S Klein, J Polesel,* Luxembourg Institute of Science and Technology, Luxembourg

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 conformality, 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 wurtzite 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 semiconducting 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 µW) 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 MOCVD, 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 3-D 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.[1] The morphology evolution of as-deposited ZnO with growth condition and parameters was systematically investigated to elucidate the major influential factors for QD synthesis by ALD. Firstly, we examined 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 ZnO 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 and widely tunable defect-emissions from red/yellow to NUV band, together with good quantum yield (maximum 97.3% at 395 nm) and excellent temperature stability. In addition, the possibility of further modifying the surface state of the as-deposited QDs by coating other materials or post-treatment are explored, and the device implementation issue for ALD QDs is also discussed.

Reference

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

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