ALD Fundamentals
Room Van Eyck - Session AF2-MoM2
High Aspect Ratio/High Surface Area/Powder ALD

Moderators: Jolien Dendooven, Ghent University, Belgium, Juhani Taskinen, Picosun Oy

10:45am **AF2-MoM2-1 Influence of the High Aspect Ratio Geometry to ALD Thin Film Growth*, Oili Ylivaara,*** VTT Technical Research Centre of Finland*; M. Utriainen, P. Hyttinen,* Chipmetrics Oy, Finland*; R. Puurunen,* Aalto University Aalto School of Chemical Engineering, Finland

ALD is a thin film growth method enabling device down-scaling beyond Moore's law[1]. Device down-scaling gives boundary conditions to thin film quality in a sense of film uniformity, conformality and homogeneity, which need to be characterized even a few nanometers thin. Shrinking device dimensions and film thicknesses set new challenges to process development and quality control as thin film analysis and characterization becomes challenging. PillarHall™ LHAR test structure has proven its value in ALD conformality characterization[2-4]. High aspect ratio (HAR) geometry in PillarHall has characteristically infinitely wide trench with height of 500 nm and width of 10 mm. However, in real applications the geometry and pitch size vary. The question is how variable HAR geometries correlate with PillarHall in conformality and ALD growth analyses? In this study, we used nanolaminate ALD process and set of variable high aspect ratio test structure geometries as substrates. Thermal ALD Al_2O_3-TiO_2 nanolaminate growth was studied at three different temperatures, at 110, 200 and 300 °C. Targeted film thickness was 25 nm. For nanolaminate, sublayer thicknesses were targeted to 1 nm both for Al_2O_3 and TiO_2. For comparison results were compared with LHAR chips coated with reference ALD Al_2O_3 grown at 300 °C. Five different conformality test chip designs were coated in a one run and analyzed: PillarHall LHAR4 with three different channel heights namely 100, 500 and 2000 nm. A prototype PillarHall LHAR3 test chip with narrow lateral channels widths from 2 to 78 µm (so called FIN-design) and vertical HAR (VHAR) test structure of an array of vertical pores, 1 µm in diameter and 219 µm in depth. During the coating chips were place in center of the wafer holder to minimize the conformality variation at the wafer surface level. After the coating LHAR samples were analyzed by optical microscopy, spectroscopic reflectometry, and for VHAR samples electron microscopy cross-section was used. We show that with PillarHall, we can study in more detail the film growth in the channel, geometry dependence and study the process saturation in the channel. We also study of applicability of narrow channels of FIN-design, width from 2 to 78 µm, and compare the results with the Gordon model[5].

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11:00am **AF2-MoM2-2 Ultra-Low Temperature ALD of Pure Antimony for Grain Boundary Engineering of Thermoelectric Materials*, Amin Bahrami,*** *S. He, R. He, S. Lehmann, K. Nielsch,* Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden e. V., Germany

Antimony (Sb) in thin film form is considered as a nano-optical material which is of interest for potential applications, such as photonic computing or high-speed holographic displays. It has been used as lens material in super-resolution near-field structures and broadband saturable absorber among others. In addition to optoelectronic properties, Sb is widely used as a dopant in tuning the transport properties of many thermoelectric materials such as PbTe, Half-Heusler compounds and so on. In this study we propose new ALD formulation for low temperature deposition of pure Sb down to 70 °C making this process applicable on the surface modification of low and medium temperature thermoelectric materials such as Mg_2Sb_3, Bi_2Te_3. Pure and conformal thin films of elemental Sb were prepared by ALD using $Sb(OEt)_3$ and $(Et_3Si)_3Sb$ as precursors with a growth per cycle (GPC) of 0.18 Å at deposition temperature of 70 °C. The electrical conductivity of the films grown on mica at 70 °C (1.13´10^4 S/cm) is slightly higher than that of reported by Pore *et al.* (1.07´10^4 S/cm). NbFeSb half-Heusler particles were successfully coated with ultra-thin layer of Sb and consolidated using high pressure sintering techniques. The results show addition of few atomic layer of Sb on NbFeSb particles can significantly enhance the electrical conductivity of the studied half-Heusler compound which was reduced during the high-pressure sintering.

11:15am **AF2-MoM2-3 Infilling Macroscopic Nanoparticle Networks via ALD*, Benjamin Greenberg*,** *K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Nanocomposites formed by infilling nanoparticle networks have unique thermal, mechanical, optical, and electronic properties. Typically, the networks are substrate-supported nanoparticle thin films with thickness on the order of 1 µm or less, and infilling is accomplished via ALD precursor dose times on the order of 1 s. In this work, we investigate the infilling of nanoparticle networks that are at least 1,000 times thicker. We press metal oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with >1 mm thickness and ~50% solid volume fraction, and we coat the pores with ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for several minutes per half-cycle. For comparison, we also produce an alternative nanocomposite by first coating the metal oxide nanopowder with ZnO in a particle ALD rotary reactor and then pressing the resultant core/shell nanopowder into a porous compact. In both cases, we use scanning electron microscopy, energy-dispersive X-ray spectroscopy, and electrical conductivity measurements to evaluate the uniformity and connectivity of the ZnO networks that form within the nanocomposites. Additionally, we examine ALD precursor diffusion and reaction kinetics and estimate saturation times through analysis of the deposition chamber pressure traces, and we compare our empirical findings to predictions based on a Knudsen diffusion model.

11:30am **AF2-MoM2-4 Zinc Acetylacetonate on Mesoporous Supports by Atomic Layer Deposition*, Jihong Yim*,** *E. Haimi,* Aalto University, Finland*; M. Mäntymäki,* University of Helsinki, Finland*; V. Kärkäs,* Aalto University, Finland*; R. Bes,* University of Helsinki, Finland*; A. Arandia, J. Velasco, T. Viinikainen,* Aalto University, Finland*; S. Huotari,* University of Helsinki, Finland*; R. Karinen,* Aalto University, Finland*; M. Putkonen,* University of Helsinki, Finland*; R. Puurunen,* Aalto University, Finland

The self-terminating nature of atomic layer deposition (ALD) enables the preparation of uniform coatings on high-surface-area materials.[1] Our general aim is to use ALD to prepare zinc promoted heterogeneous catalysts for carbon dioxide hydrogenation into methanol.[2] In this work, we aimed to obtain uniform coating of zinc on mesoporous monoclinic zirconia and gamma alumina particles in a fixed-bed flow-type ALD reactor.

Zinc acetylacetonate [$Zn(acac)_2$], a non-toxic reactant with a good stability in air, was used as an ALD reactant. Thermogravimetric analysis confirmed $Zn(acac)_2$ to be a potential reactant. $Zn(acac)_2$ was vaporized at 120 °C and carried by N_2 to the calcined support for 3 h. For zirconia, the effect of the calcination temperature (400 to 1000 °C, typically 600 °C), process temperature (160 to 240 °C, typically 200 °C), and number of cycles (1-3, 2nd reactant: oxygen) on zinc loading were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). For zirconia and alumina, the amount of $Zn(acac)_2$ evaporated was varied. Zinc distribution within a solid support particle was analyzed by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Fig. 1 and Fig. 2 of the supplementary information). A diffusion-reaction model[3,4] was used to simulate the saturation profile of zinc within theoretical pores (Fig. 3). Electronic structure of zinc was analyzed by X-ray absorption spectroscopy (XAS). The oxidation of acac ligands on the samples was observed by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with mass spectrometry (MS). The zinc content on zirconia saturated to ca. 1.3 wt-% (2.2 Zn nm^{-2}) with increasing amount of $Zn(acac)_2$. The zinc content decreased from ca. 2.2 to 0.3 wt-% with increasing calcination temperature, most likely resulting from the decreasing zirconia surface area. The zinc areal number density (ca. 2.2 Zn nm^{-2}) remained almost constant.

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11:45am **AF2-MoM2-5 Synthesis of High Surface Area Metal Oxide Catalyst Supports***, **Robert Baumgarten**, P. Ingale, K. Knemeyer, R. Naumann d'Alnoncourt, M. Driess,* BasCat – UniCat BASF JointLab, Technische Universität Berlin, Germany*; F. Rosowski ,* BASF SE, Process Research and Chemical Engineering, Germany

Group 13 metal oxides (e.g. Al_2O_3, Ga_2O_3 and In_2O_3) are utilized for a broad range of electronic applications such as semiconductors, optoelectronics and sensors. Besides, they represent essential components of heterogenous catalysts. Al_2O_3 is employed industrially as support material or catalyst itself for various reactions like epoxidation of alkenes and dehydration of alcohols [1]. Moreover, Ga_2O_3 has been intensively studied for the dehydrogenation of light alkanes and In_2O_3 catalysts gained a lot of attention due to the ability of converting CO_2 into methanol [2, 3].

In heterogeneous catalysis, reactions mostly occur at active sites on the material's surface. Therefore, high surface area and homogeneous dispersion of deposited interfaces (e.g. metal oxides) are decisive for enhanced activity [4]. Yet, standard synthesis techniques like impregnation and precipitation often lead to unwanted agglomeration. One well-established technique which overcomes uncontrolled coating is atomic layer deposition (ALD). ALD leads to uniform, nanoscale films on a materials surface and is therefore progressively attracting attention as potential synthesis-tool for catalysts [5]. However, most ALD investigations target flat substrates whereas for catalyst synthesis, powders with high surface area and porosity are demanded.

In order to enable the full potential of ALD-synthesized catalysts, the deposition behavior on porous powders has to be further elucidated. Previously, we demonstrated the growth behavior of AlO_x on mesoporous silica using the ALD process of trimethylaluminum and water [6]. In the current study, we approach other catalytically active oxides of group 13 metals like gallium (GaO_x) and indium (InO_x). Both oxides were deposited on high surface area silica powder *via* ALD and their growth behavior was studied intensively using *in-situ* thermogravimetry, XRD, STEM, FTIR and NMR. Furthermore, both processes were compared to the powder ALD process of AlO_x and reference samples prepared *via* incipient wetness impregnation.

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12:00pm **AF2-MoM2-6 ALD on Porous Substrates: From General Formulation to Fibrous Substrates and Scaling Laws***, **Wojciech Szmyt**, C. Guerra-Nuñez,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; L. Huber,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; C. Dransfeld,* TU Delft, Netherlands*; I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

In order to achieve the uniform coating in the ALD process, a sufficient gas exposure (exposure time and gas concentration) needs to be provided. This requirement becomes particularly relevant for highly porous and high aspect-ratio substrates, where the gas transport into the substrate structure is limited by diffusion (diffusion-limited regime), or for ALD precursor systems exhibiting low surface reaction rate (reaction-limited regime). This work (Szmyt *et al.*, Chem. Mat. 2022, 34, 1, 203-216) reports how the distinction between diffusion- and reaction-limited ALD regimes is directly quantitatively related to the width of the reaction front and the profile of chemisorption coverage in a single cycle ALD, all of them being determined by the natural length unit of the system. We introduce a new parametrization of the system based on its natural system of units, dictated by the scales of the physical phenomena governing the process. We present a range of scaling laws valid for a general porous substrate, which scale intuitively with the natural units of the system. The scaling laws describe (i) the coating depth in a diffusion-limited regime with respect to the gas exposure, (ii) the chemisorption coverage in a reaction-limited regime with respect to the gas exposure, and (iii) the width of the reaction front in the diffusion-limited regime. For the first time, the distinction between diffusion- and reaction-limited ALD regimes is directly quantitatively related to the width of the reaction front and the profile of chemisorption coverage in a single cycle ALD. The model system for the multicycle diffusion-limited coating of random fibrous mats was validated with an experiment of ALD on a forest of tortuous carbon nanotubes (CNTs).

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