ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-WeM
High Aspects

Moderator: Prof. Riikka Puurunen, Aalto University, Finland

10:45am **AF2-WeM-12 Preparation and Characterization of Well-Defined Mixed-Oxide and Metal-Oxide Interfaces in Porous Catalysts using ALD***, **Francisco Zaera**,* Department of Chemistry

As the chemistry of solids is in most instances determined by the nature of their surfaces, control over the nature of surface sites during preparation is critical to the design of materials for specific applications. This is a difficult task, especially when complex multicomponent atomic ensembles are required. In this presentation we illustrate how atomic layer deposition (ALD) may be used to prepare such sites, with a particular focus on the design of unique mixed-oxide and metal-oxide interfaces for catalysis.

First, we will provide details on the deposition and characterization of alumina and titania films on SBA-15, a silica support with well-defined nm-sized one-dimensional pores, and for the growth of silica films on alumina supports. Specific issues related to ALD on porous solids will be highlighted, including possible incomplete deposition inside the pores and possible precursor condensation and pore clogging.

Characterization of the deposition process and the resulting oxide films will be presented, with emphasis on the use of pore size distributions, pore area and pore volumedata from N_2 adsorption-desorption isotherms to follow the rate and quality of the film growing process. The assessment of the initial nucleation steps using NMR will also be introduced, and a discussion on the crystallinity and optical properties of the resulting films will be provided. The quantitative determination of the evolution of the surface hydroxide sites that act as nucleation centers using infrared absorption spectroscopy (IR) will be illustrated.

The unique properties of the mixed-oxide surfaces produced via ALD will be discussed. These include the creation of new Lewis and Brønsted acid sites, which can be titrated by using IR, and the ability of the new surface sites to undergo facile and reversible reduction-oxidation interconversions, as seen by IR-based CO titrations as well as by EPR spectroscopy.

Finally, new catalysts were made by adding nanoparticles of metals such as gold or platinum into these ALD-made mixed-oxide solids, either before or after the ALD. The final products were tested for reactions such as CO oxidation and the selective hydrogenation of CO_2 and of unsaturated aldehydes. In all cases, optimum catalytic performance was observed at half a monolayer of the coverage of the new oxide, strongly suggesting that the active catalytic sites may be comprised of mixed oxide local structures involving Si–O–Ti or Si–O–Al bonds. It is thanks to the sub-monolayer control of the thickness of the deposited films that such optimum catalytic performances could be attained.

11:00am **AF2-WeM-13 A Toolbox for Characterization of Film Penetration Depth in High Aspect Ratio Structures***, **Anish Philip**, M. Utriainen, J. Kinnunen, P. Hyttinen,* Chipmetrics Ltd, Finland*; V. Korpelainen, B. Sauvet,* VTT Technical Research Centre of Finland*; W. Kessels, M. Poll, B. Macco,* Eindhoven University of Technology, The Netherlands

3D semiconductor devices have often dry etched vertical high aspect ratio holes, with 20 -200 nm critical dimensions. Conformality of the ALD/CVD thin film process in those high aspect ratio (HAR) structures is important for the functionality of the devices. HAR structures can be either lateral (LHAR) or vertical (VHAR). In this study, we focused on two less known factors of ALD growth in HAR structures, namely difference between vertical and lateral HAR geometries as well as the effect of the surface roughness. The PillarHall® lateral high aspect ratio (LHAR) test structure and measurement method is an effective way for fast and easy conformality characterization of the thin film processes[1]. PillarHall LHAR is a wide trench with nominal gap height 500 nm.The unique feature of PillarHall LHAR-method is an accurate and repeatable film penetration depth (PD) profile that allows to quantify step coverage for any aspect ratio as well as to characterize reaction kinetics in the sub-micrometre dimensions and molecular diffusion conditions. The compared HAR structures (Fig.1) were on commercial test chips VHAR1 (vertical holes) and PillarHall LHAR4 (lateral trenches) by Chipmetrics Ltd, as well as a modified version of LHAR chip (M-LHAR). The ALD process used in this study was TMA/H_2O Al_2O_3 at 300 °C in Beneq TFS-200. The Gordon model [2] is a useful approach to compare and predict the film PD performance in both HAR structure types. According to Gordon model, all structures had the same feature dimensions while their roughness varied. An inverse relationship between surface roughness and PD was revealed as the measured PD was highest for M-LHAR (Rq=0.17 nm) and lowest for VHAR1 (Rq=4.8 nm). The results indicate that surface roughness together with HAR geometry and gap height are the important factors that affects the model accuracy. In this study, NIR optical reflectometry was used to precisely measure the lateral trench gap height. We show also initial results from highly sensitive and PillarHall compatible measurement tools, such as contrast imaging SEM, UV-reflectometer (Fig.2) and imaging ellipsometer. They enable to measure PD of ultra-thin films with thickness < 10 nm. The presented toolkit concept is an efficient platform consisting of several well-specified test chips, measurement instruments, and modelling tools to execute highly accurate and repeatable film penetration depth analyses of ALD processes.

References

1. J. Yim and O. M. E. Ylivaara et al., Phys. Chem. Chem. Phys., 22 (2020), 23107
2. R. G. Gordon et al., Chem. Vap. Deposition, 9 (2003),73

11:15am **AF2-WeM-14 Understanding Process Parameters of ALD on Silica Aerogels and Their Effects on Mechanical Properties***, **Victor Vogt**, A. Gayle, Z. Berquist, A. Manon, A. Lenert, N. Dasgupta,* University of Michigan

Atomic layer deposition (ALD) is a powerful tool to modify ultra-high-aspect-ratio structures with unparalleled conformality. We have recently demonstrated the ability of ALD to modify silica aerogels with aspect ratios greater than 60,000:1 and improve their thermal stability from ~600°C to ~800°C, for applications in concentrated solar thermal energy generation.[1] To facilitate conformal ALD modifications on these extreme aspect ratios, a reaction-diffusion model was developed to precisely predict infiltration into the aerogel as a function of exposure time and number of doses, enabling tunable control of the infiltration depth.[2] To build upon this work, in this study, we examine the impact of key process parameters, including deposition temperature, precursor temperature, and purging procedures, and quantify the manufacturing tradeoffs between total ALD process time and precursor utilization. Additionally, we quantify the impacts of ALD modification on the optical, thermal, and mechanical properties of silica aerogels, which are critical for their usage in solar thermal applications.

In this study, we have built upon our previous reaction-diffusion model to explore the effects of deposition temperature, precursor temperature, and purging procedure on throughput and precursor utilization. A non-intuitive inverse relationship is observed between deposition temperature and infiltration depth, which is attributed to ideal-gas-law effects on precursor dosing, and this relationship is confirmed experimentally. Next, the impact of single cycle alumina-based modifications on mechanical properties is explored through 3-point bend and compression testing, including localized strain mapping via digital image correlation (DIC). The ALD modification is found to increase the elastic modulus of silica aerogels, and the results are compared with density scaling relationships for bare silica aerogels established in literature. Understanding the effect of ALD modification on aerogel mechanical properties is critical to implementation in engineering applications and provides a potential new pathway to tailoring the mechanical properties of aerogels and other high aspect-ratio structures.

References:

[1] Z.J. Berquist, A.J. Gayle, N.P. Dasgupta, and A. Lenert, Transparent Refractory Aerogels for Efficient Spectral Control in High-Temperature Solar Power Generation. *Adv. Funct. Mater.* **2022** *32*, 2108774.

[2] A.J. Gayle, Z.J. Berquist, Y. Chen, A.J. Hill, J.Y. Hoffman, A.R. Bielinski, A. Lenert, and N.P. Dasgupta, Tunable Atomic Layer Deposition into Ultra-High-Aspect-Ratio (>60000:1) Aerogel Monoliths Enabled by Transport Modeling, *Chem. Mater.* **2021** *33* (14), 5572-5583.

11:30am **AF2-WeM-15 Tuning Properties of ZnO Deposited via ALD for Applications in Sensing and Porous Material Development***, A. Coclite, **Lisanne Demelius**,* Graz University of Technology, Austria **INVITED**

The material properties and application related to zinc oxide, ZnO,have been heavily researched for decades and still produces new scientific output every year. ZnO is characterized by versatile and unique material properties that are an asset for applications ranging from cosmetics to optoelectronics. Emerging applications employ ZnO in transparent conductive oxides or piezoelectric nanogenerators. In particular, atomic layer deposition allows to deposit ZnO with a preferential orientation, which depends on the growth temperature and is directly liked to its piezoelectricity. In this talk, an example of application of piezoelectric ZnO deposited from ALD will be shown for sensing. A force, humidity and temperature responsive electronic skin will be presented, obtained by combining piezoelectric ZnO and a thermoresponsive hydrogel into core-shell nanostructures using ALD and initiated chemical vapor deposition.

In addition, introducing porosity to ZnO thin films increases the performance drastically and opens up new fields of applications. Different methods were used to deposit porous ZnO i.e., ALD growth in non-saturated conditions or by using organic spacers which were subsequently eliminated by calcination. In-situ ellipsometric porosimetry showed that films with porosity up to 24% were obtained. Metal-organic frameworks of ZIF-8 were synthesized by subjecting porous ZnO thin films to a 2-methylimidazole vapor. The impact of the porosity of the ZnO films onto the resulting ZIF-8 layers will be shown. Our results provide new insight into the link between deposition parameters of PE-ALD deposited ZnO and properties of the resulting ZIF-8 thin films – namely crystallographic orientation, thickness, coverage and roughness – thus making it possible to tailor them towards specific applications.

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