ALD Fundamentals
Room 116-118 - Session AF2-TuA
High Aspect Ratio

Moderators: Scott Clendenning, Intel Corporation, Han-Bo-Ram Lee, Incheon National University

4:00pm **AF2-TuA-11 Modeling the Infiltration Kinetics of Porous, High Surface Area Materials in ALD: Effective Diffusivities, Saturation Times, and Densification***, **Angel Yanguas-Gil**, J Elam,* Argonne National Laboratory

Understanding the infiltration dynamics in high surface area materials is crucial to evaluate the scale up of ALD processes involving the functionalization or densification of these materials. One of the challenges in ALD is that, due to the time dependent nature of the chemistry, modelling infiltration involves three very different timescales: the timescale of the transport of individual species inside high surface area materials, the surface kinetics, and the evolution of the internal porosity with the number of cycles.

In this work we apply an approach that we have recently developed to model ALD infiltration on disordered porous materials. Based on the treatment of the reactive transport of ALD precursors and other gas phase species as a Markov chain, the model allows us to obtain local sticking probabilities in a very efficient manner. Our simulation consists of two steps: we first generate random structures through the simulation of a particle sedimentation process, with various degrees of freedom to allow for the formation of materials with different porosity and pore size distribution, as well as their inverse structures. We then use these substrates as a starting point to model both the reactive transport of gas phase species within the porous material, and the evolution of the densification process as the ALD coatings grow to fill the pores.

Finally, we also model the impact of ALD processes on the electronic properties of the resulting scaffolds: using the simulated, coated structures as a starting point, we have modeled the carrier transport efficiency of a hypothetical nanostructured electrode under two assumptions: one in which charge transport is enhanced via ALD infiltration, and a second in which the simulated coating acts as a passivation layer reducing recombination.

4:15pm **AF2-TuA-12 Thin Film Conformality Analysis, Reliability and Modeling using All-silicon Lateral High Aspect Ratio Structures***, **Oili Ylivaara**, M Ylilammi, V Korpelainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland

Device downscaling in semiconductor and microelectromechanical device industry brings new challenges from the process perspective as increased three-dimensionality sets demands towards higher aspect ratio structures which have to be filled conformably. Atomic layer deposition (ALD), based on the use of repeated, self-terminating reactions of typically at least two compatible reactants on a solid substrate, is a promising technique especially from the conformality point of view. Traditionally thin film conformality has been analysed with cross sectional specimens. Our approach is to turn the analysis to horizontal plane with all-silicon lateral high aspect ratio structures (LHAR) and reflectometry line-scans.

This work continues on earlier work on conformality analysis [1–6]. The LHAR structures consist of a lateral gap of typically 500 nm in height while the gap length varies from 1 to 5000 µm, giving aspect ratios of 2:1 to 10 000:1. LHAR chips were coated with ALD Al_2O_3 and TiO_2 films, the effects of pulse and purge times were inspected from conformality point of view, and the measurement reliability was characterized with atomic force microscopy and QuickVision optical coordinate measuring tool. Diffusion model [6] was used to study the propagation of the ALD growth in the narrow channel. According to reflectometry measurements longer pulse time increased the penetration depth of the film to the narrow channel. The diffusion model was well in agreement with the experimental results. Measurement reliability and uncertainty components of the measurement were studied systematically. Therefore realistic uncertainty estimates can be given for the results. The LHAR structures presented here with thin film analysis and theoretical diffusion model accelerate the process up-scaling from small to large industrial scale.

Acknowledgements: Funding for this work comes from Academy of Finland's Finnish Centre of Excellence in Atomic Layer Deposition and Tekes PillarHall project.

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[5] Korpelainen et al., Traceability of internal length scale in PillarHall thin film conformality test chips. 5th Dresden Nanoanalysis Symposium "In-situ Microscopy"; 1 September 2017, Dresden, Germany

[6] Ylilammi et al. to be published

4:30pm **AF2-TuA-13 High Step Coverage Properties of New Zr Precursors with High Thermal Stability for High-k***, **Haeng-Don Lim**, S Jeon, J Cho, W Chae, J Park, S Yim, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

New Zr precursors have been developed using a tri-amine structure with enhanced thermal stability. Currently precursors of Cyclopentadienyl structure (Cp-Zr), which have high thermal stability, are used as precursors of ZrO_2 thin films. We synthesize Zr precursors of tri-amine structure (ZTA-01) with further improved thermal stability, and analyze characteristics according to structure difference with Cp structure.

The ALD window of ZTA-01 is 220 to 320℃ (Fig. 1(b)). Compared with Cp-Zr, the high-temperature stability of ZTA-01 was found to be about 20℃ higher. As a result of XRD analysis, distinct tetragonal peaks of ZrO_2 were clearly observed at 310℃ (Fig. 2). The stoichiometric ratio of O / Zr was found to be close to ideal ZrO_2 (O / Zr = 2.00) with ZTA-01 of 1.96 by XPS at 310℃. Impurities C and N were not detected.

The hole structure pattern of aspect ratio 60-65: 1 is used and the step coverage characteristics are analyzed at the ALD window temperature of 290 ~ 330℃ of ZTA-01. (Fig. 3) The step coverage is 97% at wafer temperature 290℃, 98% at 300℃, 99% at 310℃, 97% at 320℃, and 94% at 330℃. The ZTA-01 step coverage in the ALD window is more than 97 to 99%, which is evidence of the high thermal stability of ZTA-01 and the ideal self-limited reaction. Under the same conditions, the step coverage characteristic of the ZrO_2 thin film using Cp-Zr is 90% (Fig. 4(a)). This experiment shows that the Zr precursors of the tri-amine series are improved by at least 8% in the step coverage characteristics when compared with the Zr precursors of the cyclopentadienyl structure. Similar to the step coverage characteristic of ZrO_2 single layer using ZTA-01, the step coverage characteristic is 99% even in ZAZ laminated structure for reducing the leakage current (Fig. 4(b)).

This result shows that the inter-molecular stability and the intra-molecular stability of the Tri-amine structure are all high, so that it is not subjected to thermal decomposition to the bottom of the high aspect ratio and shows step coverage of 99% through a self-limited reaction.

4:45pm **AF2-TuA-14 Atomic Layer Deposition: Tailoring High Aspect Ratio TiO_2 Nanostructures***, **Raul Zazpe**, H Sopha, J Prikryl, M Krbal, J Macak,* University of Pardubice, Czech Republic

The ongoing advances in the fabrication techniques over the last decades have allowed the shrinking of the devices to nanoscale dimensions, yielding a new generation of promising nanostructures as nanowires, nanorods or nanotubes. Among such nanostructures, anodic self-organized 1D TiO_2 nanotube layers have received significant scientific and technological interest, motivated by the semiconductive nature of the TiO_2, unique tubular architecture, chemical and mechanical stability, unidirectional electron transport through nanotube walls, biocompatibility, as well as simple and low cost fabrication process.[1,2]

An encouraging further step lies on the fabrication of TiO_2 nanotubular composite structures with new functionalities by the deposition of secondary materials. However, the shrinking to nanoscale dimensions brings the challenge of attaining conformal, homogeneous and continuous secondary material coatings. Conventional thin film deposition methods result inefficient and display serious limitations for the secondary material coating of high aspect-ratio nanostructures.[3] To date, atomic layer deposition (ALD) is the only deposition method capable to deposit continuous and conformal layers into high aspect-ratio nanostructures with an unprecedented sub-nanometer thickness control.[4] Thus, TiO_2 nanotubular composite structures have been produced via ALD by the deposition of ultrathin films of materials as TiO_2,[5] Al_2O_3,[6] ZnO,[7,8] or CdS,[9] or homogeneous decoration with noble metal nanoparticles.[10] The composite nanostructures display synergetic effects resulting in enhanced performance in a wide range of applications, such as photocatalytic,[5] sensing,[8] solar cell,[9] catalytic,[11] and battery.[12]

The presentation will focus on fabrication and experimental details, and recent photocatalytic,[5] sensing,[8] solar cell,[9] catalytic,[10] and battery[11] reports will be presented and discussed.

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5:00pm **AF2-TuA-15 Mechanisms Limiting Conformality in Thermal and Plasma-assisted ALD Investigated by Lateral High Aspect Ratio Structures***,* ***Karsten Arts****, V Vandalon,* Eindhoven University of Technology, Netherlands*; F Gao, M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland*; E Kessels, H Knoops,* Eindhoven University of Technology, Netherlands

This work investigates the processes governing conformality achieved by ALD, using Lateral High Aspect Ratio (LHAR) test structures supplied by VTT.[1] We show that these structures are well suitable for investigating the underlying ALD chemistry, as the shape of the thickness profile and the penetration depth are indicative for the growth regime and provide insight into parameters such as sticking probabilities.

In the new PillarHall™ LHAR3 structures the reacting species diffuse underneath a removable membrane which is supported by pillars giving a 500 nm spacing. This configuration offers new possibilities compared to traditional vertical structures. Among others, top-view diagnostics can be applied to straightforwardly determine the thickness profile and material properties. A range of diagnostics is validated in this work for this top-view analysis. Moreover, the structure has features with aspect ratios up to 10000. Therefore a non-fully saturated profile is acquired for even the most conformal processes, which provides information on the limiting mechanisms.

Two cases are discussed to exemplify these possibilities. Firstly, in the case of thermal ALD of Al_2O_3 using TMA and water it is known from recent work that at low temperatures the growth is limited by the reduced reactivity of H_2O towards $–CH_3$ groups.[2] We examine how this reactivity affects the conformality, by measuring and simulating Al_2O_3 thickness profiles for different substrate temperatures. For example, at 200°C table temperature a sloping profile is observed with a half-thickness-penetration-depth (HTPD) of ~400 µm (AR=800). This profile seems to be consistent with the low sticking probability of water at these temperatures ($s \sim 3 \cdot 10^{-5}$).[2] That is, from Monte Carlo simulations a growth regime in between reaction-limited and diffusion-limited growth is expected for this sticking probability and penetration depth, yielding such a sloping profile.

Secondly, in the case of plasma-assisted ALD of Al_2O_3 recombination-limited growth is observed, as the HTPD is reduced to ~30 µm (AR=60) through recombination of the reactive O radicals. As even these short profiles can be resolved using top-view diagnostics, the LHAR3 structures can be employed to investigate recombination probabilities in plasma-assisted ALD as well. On the basis of the aforementioned studies, these and other insights into ALD chemistry relevant to conformal growth will be provided.

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5:15pm **AF2-TuA-16 Multilayers on Reinforcement Fiber Fabrics with ALD***,* ***Pauline Dill****, F Pachel, M Scharf, W Goedel,* Chemnitz University of Technology, Germany

Carbon fiber fabrics, with a size of 30x8 cm, were coated smooth in a homebuilt reactor with combinations of three different ALD-layers. We used inorganic ALD coating (Al_2O_3, TiO_2, $Ti_3(PO_4)_4$) as well as an organic-inorganic TiO_2/furfuryl alcohol coating.[1] The coatings were combined in such a way that stacks of inorganic/organic-inorganic/inorganic were produced. The layer thickness and the homogeneity of each layer and the combination of the three layers were investigated with scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The elemental analysis of the coating was investigated with energy-dispersive X-ray spectroscopy (EDXS). The coated fabrics will be embedded in a ceramic matrix to give a fiber reinforced ceramic, in which the coating should provide oxidation protection for carbon fibers and also the coating may be helpful for crack deflection in the composite. Each of the coating in the combination has at least one task to protect the carbon fiber in the ceramic matrix composites. The first coating should protect the fiber from oxidation environment, the second one is needed for crack deflection and the top coating is needed to protect the remaining coated carbon fiber fabrics, when it will be sintered at high temperatur. For good crack deflection the three coatings should not stick too tight to each other, so that the fiber is able to move along the fiber axis. The delamination behavior of the coatings was also seen in SEM images.

References:

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