

Late-breaking Abstracts

Room Grand Ballroom A-C - Session LB1-WeA

Late Breaking ALD

Moderator: Dr. Sumit Agarwal, Colorado School of Mines

1:45pm LB1-WeA-2 Recent Advances for Spatial Atomic Layer Deposition Process: Microreactor Direct Atomic Layer Processing (μ DALP™), Maksym Plakhotnyuk, A. Varga, I. Kundrata, ATLANT 3D, Denmark; J. Bachmann, FreFriedrich-Alexander Universität, Germany

In parallel to additive manufacturing leading the revolution in traditional manufacturing, the same principles can revolutionize traditional thin film deposition techniques. Where lithography and vapor phase deposition techniques struggle, for example, with rapid iterations for prototyping or incompatibility with the used chemistry, additive manufacturing can shine. Indeed, several approaches are in development for 3D nanoprinting^{1,2,3}.

Atomic Layer Deposition, and in more general Atomic Layer Processing, offers a unique opportunity for localized 3D processing/printing due to its two-step process. While simple in theory, due to well-developed examples of Spatial Atomic Layer Deposition (SALD), in practice miniturization of SALD requires substantial effort into the creation of suitable micro-nozzles. Uniquely, ATLANT 3D has developed proprietary Spatial ALD micronozzles, naming the process microreactor Direct Atomic Layer Processing - μ DALP™.

In recent years, the team at ATLANT 3D has been able to significantly develop the technology to reduce the μ DALP™ resolution, increase material capabilities, assessable morphologies, and new instruments. Giving one example of recent development in morphologies; films deposited with μ DALP™ have conformal coverage of gratings, microchannels and trenches up to a depth of 25 μ m using a Platinum deposition process (Figure 1). Substrates with a surface roughness including Carbon nanograss (Figure 2), black silicon and anodized Aluminum Oxide membranes were also conformally coated with roughness up to an aspect ratio of 1:25 again with Platinum and TiO₂. Our results demonstrate how a given ALD material process (in this case, Pt and TiO₂) can be used with ATLANT 3D technology to deposit localized area conformal coatings of complex surfaces with an aspect ratio of 1:25. The μ DALP™ technology enables rapid prototyping and manufacturing for an array of applications from sensors (temperature, pressure, gas sensing and capacitive) to optics, all with sensitivities that meet or exceed those of devices made using conventional vapor phase deposition techniques.⁴ In addition, rapid localized processing facilitated by ATLANT 3D technology of such devices enables design innovation and optimization not possible with other thin film deposition techniques and lithography.

[1] Kundrata I. et al., *ALD/ALE 2022 [Int. Conf.]*, 2022

[2] de la Huerta C. A. M. et al., *arXiv*, 2020, 0523.

[3] Winkler, R. et al., *J. Appl. Phys.*, 2019, 125, 210901

[4] Kundrata I., et al., *Small Methods.*, 2022, 6 (5), 2101546

2:00pm LB1-WeA-3 Towards Improved Conversion of Wet Waste to Jet Fuel with Atomic Layer Deposition-Coated Hydrodeoxygenation Catalysts, W. Wilson McNeary, J. Miller, S. Tacey, National Renewable Energy Laboratory; J. Travis, Forge Nano; M. Griffin, K. Jungjohann, G. Teeter, National Renewable Energy Laboratory; T. Eralp Erden, Johnson Matthey, UK; C. Farberow, National Renewable Energy Laboratory; L. Tuxworth, M. Watson, Johnson Matthey, UK; A. Dameron, Forge Nano; D. Vardon, Alder Fuels

The U.S. aviation sector has set a target for 50% reduction in CO₂ emissions by 2050 (vs. 2005 levels) which will require rapid, large-scale deployment of sustainable aviation fuel (SAF). State-of-the-art SAF production relies on hydrotreating esters and fatty acids (HEFA); however, this pathway is limited by insufficient supplies of esters and fatty acids to meet future jet fuel demand, relatively high feedstock cost, and, in some cases, direct competition with food crops. Wet waste (e.g., food waste, animal manure, wastewater sludge) represents an untapped domestic resource, as most of the wet waste generated annually in the U.S., which contains more than 1.3 petajoules (10¹⁵ J) of energy, is either landfilled or fed to anaerobic digestors to make biogas for heat and/or electricity. To broaden the pool of renewable carbon sources available for SAF production and avoid the drawbacks of the HEFA pathway, wet waste may instead be harnessed as a SAF feedstock.

The conversion of wet waste-derived volatile fatty acids (VFAs) into jet fuel-range hydrocarbons is a promising route for increasing SAF production; *Wednesday Afternoon, July 26, 2023*

however, the cost and moderate alkane selectivity of Pt-based hydrodeoxygenation (HDO) catalysts present challenges for commercialization. To address this, we used atomic layer deposition to apply TiO₂ overcoats to Pt/Al₂O₃ catalysts and create new interface sites that exhibited 8 times higher site time yield of the desirable n-alkane product than uncoated catalyst. Through a combination of temperature programmed reduction, NH₃ temperature programmed desorption, X-ray photoelectron spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, and density functional theory calculations, we found that the increased selectivity of the ALD-coated catalyst was due to the creation of O vacancies at the Pt-TiO₂ interface under reducing conditions, resulting in new Ti³⁺ acid sites near the active metal. This ALD coating strategy was used to improve the alkane selectivity of the base 0.5 wt % Pt/Al₂O₃ catalyst beyond that of an uncoated catalyst with an order-of-magnitude more Pt, which illustrates the benefit of utilizing the nanoscale precision of ALD to tailor interface sites and increase the atom efficiency of precious-metal catalysts.

2:15pm LB1-WeA-4 A Kinetic Model for Heterogeneous Nucleation in ALD and CVD, Andreas Werbrouck, S. Bent, Stanford University

As atomic layer deposition (ALD) becomes an increasingly mature technique, sound models that describe all stages of the growth are needed. Here, we develop a kinetic model for heterogeneous ALD nucleation and growth: we describe how an ALD film forms on a starting surface that is different from the steady-state growth surface, and the subsequent growth of the material after the initial surface has been covered. Understanding nucleation is relevant for any ALD process, but especially important for metal-on-dielectric deposition, where island growth is often observed, and for area-selective deposition, where nucleation on the non-growth surface is to be avoided.

Steady-state growth and precursor reaction kinetics are relatively well-understood and other models for heterogeneous nucleation have been published before. Our model, in the form of a system of differential equations, describes heterogeneous nucleation kinetics in a continuous, macroscopic way as a function of time, from initial nucleus formation to coalescence and beyond. A key element of the model is the introduction of both homogeneous and heterogeneous sticking coefficients, and a description of the perimeter of the covered part of the surface. This perimeter is dependent on the ratio of the sticking coefficients. We modeled the perimeter evolution with a changing coverage for various homogeneous and heterogeneous sticking coefficients based off Monte Carlo simulations.

In the first part of the presentation, we will discuss results of our model describing heterogeneous nucleation for chemical vapor deposition. We show that the nucleation delay depends on the interplay between the homogeneous and heterogeneous sticking coefficient. In the second part, we will extend the model to a two-precursor ALD system. Due to the use of time as a parameter, the model allows us to discern between the surface change per ALD cycle and the surface change per unit time, and we report on the effect of exposure per cycle (for both precursors) on nucleation delay and growth. Thickness and coverage results can then be compared to experiment. In the final part, we will a) link the model to earlier work on catalytic surfaces b) compare the model to literature models for ALD nucleation (Avrami equation, population balance equation) and c) fit the model to literature data. Our model allows one to describe the generation of new nuclei intuitively through the heterogeneous sticking coefficient, and to explain nucleation enhancement, delay, and breakthrough behavior, while avoiding assumptions on (hemi-)spherical particles. In future work, we will expand our model to incorporate surface diffusion and substrate geometry.

2:30pm LB1-WeA-5 Intrinsic Area Selective Atomic Layer Deposition of MoS₂ Thin Films, J. Soares, Wesley Jen, Boise State University; J. Wensel, Micron Technology; S. Hues, E. Graugnard, Boise State University

As the critical dimensions in today's semiconductor devices continue to shrink, new methods for device fabrication are paramount for continued reduction in scaling. These fabrication processes must be adaptable in order to evolve with future technology nodes and scales, while providing flexible material integration techniques within the high complexity of device structures. Area selective atomic layer deposition (ASALD) is a deposition technique that utilizes a bottom-up patterning approach for self-alignment of deposited materials. ASALD operates on the basis that functional groups either present or absent on a growth surface will promote or inhibit nucleation. This contrast can lead to selective deposition. In addition to compatible processing techniques, next

generation materials also need to be studied. Layered two-dimensional (2D) molybdenum disulfide (MoS_2) is a semiconducting material that shows great promise due to its atomically thin structure and impressive electrical properties. In this work, we report the ASALD of MoS_2 on patterned template substrates of common dielectric materials versus thermal silicon oxide and nitride. Growth and non-growth surfaces were initially screened with X-ray photoelectron spectroscopy (XPS) characterization of blanket MoS_2 films after numerous ALD cycles. The selectivity parameter between surfaces was calculated using XPS, revealing a high selectivity of $S = 0.94$ after 20 ALD cycles for growth on ALD alumina versus thermal silicon oxide. These results identified contrasting surfaces that were then patterned to investigate area selectivity. MoS_2 ALD was performed at 200 °C on patterned surfaces that were then annealed at 650 °C for 30 minutes. Samples were characterized using Raman spectroscopy maps of crystalline MoS_2 modes and time-of-flight-secondary ion mass spectroscopy (ToF-SIMS) elemental mapping, which confirmed ASALD. These results hold promise for advancing the integration of 2D materials into device manufacturing.

2:45pm LB1-WeA-6 Selective Deposition of HfO_2 on Aminosilane-treated TiN/SiO_2 Substrates, Yujin Lee, Stanford University; H. Kim, Samsung Advanced Institute of Technology, Republic of Korea; S. Bent, Stanford University

For the continued downscaling of semiconductor devices, new approaches are required to meet the fabrication challenges. Area-selective atomic layer deposition (AS-ALD) is a bottom-up fabrication process that provides a great opportunity to overcome the problems associated with current top-down fabrication processes such as cost and complexity. Toward the implementation of an AS-ALD process at the sub-10 nm level, studies on AS-ALD using small molecule inhibitors (SMIs) having angstrom level thickness have been reported. However, since SMIs contain carbon species, their use in an inhibitor layer could affect the device's characteristics such as dielectric constant and leakage current density. On the other hand, various techniques of readily-available surface treatments can be utilized to functionalize the surfaces so that they are deactivated for reducing nucleation without adding carbon species.

In this study, we develop a surface treatment process that uses an aminosilane molecule to block the adsorption of Hf precursors for HfO_2 ALD. We show that SiO_2 surfaces functionalized by the aminosilanes add only terminal $-\text{SiH}_3$ to the surface without attaching carbon species. In addition, because both standard ALD and AS-ALD processes are strongly dependent on the precursor, tuning the ALD precursor provides another variable by which selectivity may be achieved. We first investigate the effect of ALD precursor on the growth characteristics and film properties for three different Hf precursors with alkylamide, alkoxide, and halide ligands, respectively. Using these three different optimized HfO_2 ALD processes and adding surface functionalization steps, we perform AS-ALD on TiN/SiO_2 substrates. ALD blocking results show that the resulting hydride ($-\text{SiH}_3$)-functionalized SiO_2 surface can successfully inhibit the adsorption of the Hf precursor without the need for carbon species at the surface. Best results were found using the Hf alkoxide precursor, for which selectivities of greater than 80% were achieved after 30 cycles of HfO_2 ALD. This work introduces a new surface treatment together with considerations for ALD precursor selection to enable an AS-ALD process.

3:00pm LB1-WeA-7 Atomic Layer Deposited Zr-doped HfO_2 (HZO) and Indium Gallium Oxide (IGO) Thin Films for 3D Gate-All-Around FeFET, Boncheol Ku, J. Hur, J. Jeong, C. Choi, Hanyang University, Korea

Recently, HfO_2 -based ferroelectric (FE) field effect transistors (FeFETs) have gained attention for NAND flash memory applications due to their superior advantages compared to $\text{SiO}_2/\text{Si}_3\text{N}_4/\text{SiO}_2$ (ONO)-based FETs. These advantages include faster write/erase speeds, non-destructive readout, lower operation voltage, higher scalability, and CMOS compatibility. However, when FE thin films are applied to poly-Si, there can be issues such as grain-dependent threshold voltage (V_{th}) degradation and temperature-induced V_{th} instability due to the low-k interfacial layer formed at the interface between FE- HfO_2 and poly-Si. With this regard, materials system using suitable FE thin film and oxide semiconductor should be explored and corresponding device feasibility needs to be investigated. To address this, we have proposed using atomic layer deposited (ALD) FE thin film and oxide semiconductors (OS) as charge trapping layer and alternative channel, respectively, in 3D NAND architecture.

In this study, we successfully demonstrated ALD Zr-doped HfO_2 (HZO) FE thin film and an indium-gallium oxide (IGO) channel for a 3D vertical Gate-All-Around (GAA) NAND flash memory device using with gate length (L_g)

and spacer length (L_s) of 50 nm. [Fig. 1] These FE and OS thin films are adopted as an alternative charge trapping layer and channel layer alternative ONO and poly-Si, respectively. The I_d - V_g characteristic of the 3D GAA FeFET device indicates high-quality interface between the HZO and IGO thin films, with subthreshold swing of 90 mV/dec and almost no hysteresis under bias sweeping. The device shows a maximum memory window (MW) of 2.5 V, allowing for potential multilevel cell (MLC) operation. The stable sub-loop switching of ferroelectricity for MLC memory operation is an important factor, and stable 2 bits/cell retention properties up to 10^4 sec at room temperature are achieved, extrapolated to 10 years retention time. [Fig. 2]. These results suggest that ALD FE thin film and OS materials can be a promising alternative to current ONO/poly-Si materials for advanced V-NAND flash memory applications.

3:15pm LB1-WeA-8 Development of Robust Gate Insulators for MIS-HEMT Structures Based on ALD/PEALD Techniques, Messaoud Bedjaoui, S. Cadot, J. Amiran, R. Contie, A. Thiam, C. Bout, CEA/LETI-University Grenoble Alpes, France; P. Fernandes Paes Pinto Rocha, CEA/LETI-University Grenoble Alpes, Grenoble INP-LTM, France

In the past few years, AlGaIn/GaN based metal-insulator-semiconductor high-electron-mobility transistors (MIS-HEMTs) have attracted considerable interest, providing unprecedented power levels and efficiencies. The dielectric quality as well as the GaN-dielectric interface play a critical role in the performances of such devices. Atomic Layer Deposition (ALD) and Plasma Enhanced-ALD are the most suitable techniques to address the challenge of MIS gate dielectrics. As such, the Al_2O_3 layers grown by ALD are materials of choice due to high dielectric constant, high breakdown field and high conduction-band offset on GaN. However, the dielectric performances of Al_2O_3 rapidly degrade at high temperature (above 800°C) due to the crystallization. One promising strategy for high quality gate dielectrics consists in combining SiO_2 and Al_2O_3 deposits in order to prevent the dielectric crystallization.

In this work, we analyse the general performance of MIS gate dielectrics (with and without post deposition annealing or PDA) using physico-chemical (X-ray photoelectron spectroscopy, X-ray reflectometry, grazing incidence X-ray diffraction) and electrical analyses (Hg probe measurements, MOSCAPs). We primarily focused on the evaluation $\text{Al}_2\text{O}_3/\text{SiO}_2$ -based films (thickness range 20-30nm) obtained by two thermal ALD modes (300°C) on silicon substrates: (i) alternating the deposition of separate SiO_2 and Al_2O_3 layers (nanolaminated); (ii) combination of ALD super cycles allowing the formation of AlSiO_x layers.

For the ALD super cycles approach (50% SiO_2 content according to XPS analysis), XRR density and permittivity values of AlSiO_x layers are around 2.8 and 5, respectively. We outline the close correlation between the Al/Si ALD process ratio and the AlSiO_x composition. AlSiO_x layers preserve their density and permittivity values after PDA treatment unlike Al_2O_3 layers (using H_2O or O_3 oxidant, see Fig. 1 and 2). This is attributable to the fact that AlSiO_x stays amorphous up to 850°C, as revealed by GIXRD analyses (see Fig. 3). We report a drastic decrease of leakage current and an increase of breakdown field in comparison to Al_2O_3 layers before and after PDA treatment at 850°C (see Fig.4). This trend prevails for both ALD multilayer and ALD super-cycles approaches confirming the deep impact of SiO_2 fraction in the AlSiO_x layers composition and subsequently on the general electrical performances. Furthermore, preliminary evaluation of interface passivation layers (such as *in-situ* plasma clean or PEALD-deposited AlN barrier) underlines the great potential of ALD/PEALD techniques in the fabrication of robust gate insulators for AlGaIn/GaN-based HEMTs.

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