ALD Fundamentals
Room Hall 3A - Session AF1-WeM

Growth and Characterization: High Aspect Ratio/High Surface Area/Powder ALD and Characterization of ALD Films

Moderators: Noureddine Adjeroud, Luxembourg Institute of Science and Technology (LIST),, **Viljami Pore**, ASM

8:00am **AF1-WeM-1 Conformality of Ternary Oxides by Spatial ALD: Monte Carlo Simulations and Experimental Study**, ***Mike van de Poll***, *S. van der Heijden, P. Poodt, E. Kessels, B. Macco,* Eindhoven University of Technology, Netherlands

Conformal film growth is one of the key merits of ALD and essential for many applications. The conformality of binary oxide depositions using a simple AB-process has been thoroughly examined in the past and is well understood. Although materials containing three or more elements have been conformally deposited before in 3D-structures, fundamental understanding is still limited. This is especially the case for spatial ALD (s-ALD), which is promising for high-volume low-cost applications. In this work, we investigate the conformality of atmospheric-pressure s-ALD deposited ternary oxides, both through modeling and experiments.

A significant influence of the precursor dosing method (i.e., dosing the metal precursors in separate cycles within a supercycle versus co-injecting both metal precursors simultaneously) on the conformality was demonstrated using a Monte Carlo model. The supercycle method generally grants a large degree of control over the film stoichiometry because of the fact that the precursor doses can be tuned separately. To obtain films with invariable stoichiometry with respect to position in the trench, the doses should be tuned either such that either full step coverage is reached, or such that the penetration fronts of both precursors overlap. Controlling the composition is more challenging for Co-injection. Modeling results highlight the importance of many different aspects, such as precursor partial pressure, diffusivity, and sticking probability.

The modeling results were confirmed experimentally for both dosing methods by spectroscopic ellipsometry and XPS. Additionally, experimental results show the importance of precursor–precursor interactions at the surface during co-dosing. Al-doped ZnO and AlZnO were deposited in lateral high-aspect-ratio (LHAR) test chips (PillarHall™ by Chipmetrics Ltd) using DMAI, DEZ, and water. Co-injection resulted in two distinct regions: an Al-rich region at the start of the trench, followed by a Zn-rich region deeper in the trench. A detailed study revealed that DMAI displaces DEZ molecules bound to the surface, resulting initially in primarily AlO_x growth, followed by ZnO growth deeper in the trench where DMAI is depleted. Precursor displacement can potentially play a role for many other co-injection processes depending on the reactivity of the precursors.

This study into the different dosing methods of s-ALD has shown which aspects are important for conformal deposition and enables the deposition of high-quality ternary oxides in high-aspect-ratio structures.

8:15am **AF1-WeM-2 Reusable Macroscopic HAR Test Kit Enabling Fast, Routine Characterization of Film Conformality**, ***Jesse Kalliomaki***, *I. Manninen, J. Järvilehto,* Applied Materials, Finland

A defining feature of atomic layer deposition (ALD) is conformality, which has made it an invaluable tool in several industries. However, the testing film growth in high-aspect-ratio (HAR) structures has thus far been a laborious, slow, and costly endeavor, involving manual analysis of specialized nanostructures [1]. This limits the conformality studies during ALD process development.

This approach also neglects another strength ALD offers, scalability. ALD can coat macroscopic objects conformally as well as the microscopic. However, conformality tests carried out on a microscopic scale often led to overestimation of the film penetration depth at half-thickness (PD50) on macroscopic HAR objects [2], failing at the intended purpose of the ALD film.

Our work introduces a novel approach to tackle the issue of cost and scalability: a reusable HAR-test device comprising a wafer-sized annular metal disk with radial grooves of varying height (50-900 µm) extending outwards (Fig 1a). When placed on a wafer, closed lateral tunnels with varying aspect ratios are formed. After deposition, growth pattern is revealed by removing the disk (Fig 1b), easily accessible using wafer-scale instruments. Due to the macroscopic size of the pattern, low resolution techniques, such as ellipsometry or even measurement using a ruler, can be used to obtain useful results. This feature was leveraged to boost process development efficiency by varying a process parameter in steps during a deposition. This resulted in a staircase profile, comprised of characteristic PD50s of the varied parameter (Fig. 1c). For example, a TEMAHf-H2O deposition using TEMAHf pulse times of 1.0, 2.0, 2.7 & 3.0 s, resulted in PD50s of 16, 20, 22 & 23 mm, respectively, in a tunnel with a height of 240 µm. Data from 12 tunnels was combined to form the HAR Growth Constant (HGC), describing how the process scales to HAR features with any hydraulic diameter within the same flow regime.

This invention (patent pending) enables routine conformality testing during process development in a cost-effective and timely manner - facilitating further exploration of experimental conditions.

[1] Appl. Phys. Rev. 6, 021302 (2019); doi: 10.1063/1.5060967
[2] Manninen, I., Aalto University, Espoo, Finland, 2022. https://aaltodoc.aalto.fi/handle/123456789/113671 (accessed 2022-02-01).

8:30am **AF1-WeM-3 Superconformal ALD Using a Heavy Inert Diffusion Additive**, ***Arun Haridas Choolakkal***, *P. Mpofu, P. Niiranen, J. Birch, H. Pedersen,* Linköping University, Sweden

The self-limiting surface chemistry of ALD routinely allows perfectly conformal, i.e., a step coverage of 1, film deposition. However, achieving superconformal deposition, i.e., a step coverage above one, with thicker film in the bottom of a recessed feature than in the top, has remained elusive in ALD, we will here show that it is possible. We recently showed how a CVD process for boron carbide using triethyl boron as single source precursor can be perfectly conformal by adding a co-flow of Xe.[1] Here, we expand on this concept by using Kr as diffusion additive in thermal ALD of AlN from trimethyl aluminum (TMA) and ammonia (NH_3).

We observe that the step coverage in 16:1 aspect ratio feature increased from 1 to 1.4 with the addition of Kr to the ALD process. The deposition depth observed from initial depositions conducted in lateral high-aspect-ratio (LHAR) chips with 500 nm gap height shows no significant change with Kr addition, and it remainedat 42 µm.

The rationale behind this is the competitive co-diffusion of mainly the lighter NH_3 (17 amu) and Kr (83.8 amu) during every other half-cycle. The higher sticking probability of TMA ensures a chemisorbed layer up to 42 µm depth in the LHAR structure, limited by the influx of the given TMA dose. Kr, with a lesser mass difference with TMA (72 amu), does not provide a notable competitive advantage during co-diffusion. This means that NH_3 molecules are pushed down to the trench bottom, resulting in dilution at the openings of the high-aspect-ratio feature. This dilution prevents the surface saturated half-reaction at the openings while achieving an excess NH_3 concentration at the trench bottom, ensures surface saturated half-reactions at the bottom surfaces.

Reference:

A. H. Choolakkal et al. Competitive co-diffusion as a route to enhanced step coverage in chemical vapor deposition. *ChemRxiv***2024**: doi:10.26434/chemrxiv-2024-nlf00

8:45am **AF1-WeM-4 Ald of Alumina-Silica Multilayers on Carbon Microfiber Fabrics: Microstructure and Potential as Refractory Oxygen Diffusion Barriers**, ***Elise des Ligneris***, *D. Samélor,* CIRIMAT-INPT, France*; A. Sekkat,* CNRS, France*; C. Vahlas,* CIRIMAT-INPT, France*; B. Caussat,* CNRS, France

Provided that the sensitivity of carbon fibers (CFs) to thermal oxidation above 400 °C is tackled, CFs could then be used as reinforcement in high temperature composites, microwave absorption materials or thermal insulators in extreme environments [1, 2]. Indeed, CFs are not subjected to creep with increasing temperature, and exhibit even higher elongation modulus, contrary to ceramic microfibers such as SiC or boron-doped alumina [1, 2]. Rather than protecting a carbon macro-object, this study makes use of ALD for the deposition of a refractory oxygen diffusion barrier layer (OBL) on the surface of CFs (7 µm diameter) entangled within a woven fabric [1, 2]. While ALD of alumina-silica barrier layers was previously reported [3], the deposition of silica-based thin films on CFs have long been considered a challenge. Indeed, the oxidation-sensitive nature of CFs does not bode well with the thermal oxidative conditions associated with common protocols of silica ALD [3]. Nonetheless, the use of a catalytic ALD process illustrated in Scheme 1 enabled for the deposition of amorphous alumina-silica bilayers from 445 K using trimethylaluminium (TMA) and tris(*tert*-pentoxy)silanol (TPS) [2]. Amorphous alumina ALD was achieved below 120 °C using TMA and water [1]. The sequence of alumina low

temperature ALD and alumina-silica catalytic ALD allowed for the deposition of alumina-silica laminates of tunable thicknesses on CFs, as presented in Figure 1[1, 2]. A CF-alumina interface prevented from carbon diffusion within the coating, while the fluid phase of silica could fill voids induced in part by alumina crystallisation. This study then focused on the compounds formed at the alumina-silica interface, in a trial to reach a three-dimensional structured coating, containing a crystalline mullite structure oriented parallel to the carbon substrate, and thus limiting events of intra-delamination.

1. des Ligneris, E., et al., Amorphous Alumina Thin Films Deposited on Carbon Microfibers As Interface Layer for Thermal Oxidation Barriers. ACS Applied Engineering Materials, 2023. 1(10): p. 2707-2722.
2. des Ligneris, E., et al., *Catalytic ALD of alumina of amorphous alumina-silica thin films on carbon microfibers*. AVS Journal of Vacuum Science and Technology A, 2024.
3. Putkonen, M., et al., *Low-temperature atomic layer deposition of SiO2/Al2O3 multilayer structures constructed on self-standing films of cellulose nanofibrils.* Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 2018. 376(2112): p. 20170037

9:00am **AF1-WeM-5 Pillarhall Lateral High Aspect Ratio Assisted Unveiling of Secondary Growth Front and Background Reaction Mechanism in Atomic Layer Deposition***, A. Philip,* Chipmetrics Ltd, Finland*; S. Elliott,* Schrödinger, Germany*;* ***Jussi Kinnunen****,* Chipmetrics Ltd, Finland*; A. Mirhamed,* Park Systems GmbH, Germany*; M. Zaheer, M. Utriainen,* Chipmetrics Ltd, Finland

The 3D vertical scaling trend in nanoelectronics necessitates high-aspect ratio (HAR) features and conformal ultra-thin films, crucial for the semiconductor industry today. The lateral high aspect ratio (LHAR) test structure and measurement method is a unique test vehicle for characterizing the conformality for the 3D thin films. The unique feature of LHAR is the ability to quantify the conformality for both ALD and CVD processes. PillarHall® LHAR4 test chips enable accurate and repeatable film penetration depth (PD) profile measurements which help to predict and quantify the step coverage in any HAR features. In the current research we are showing another important aspect of these LHAR beyond the already existing applications. Utilization of LHAR in understanding the reaction mechanism of ALD process especially in 3D structures is the major highlight of the current research. We reveal a secondary reaction front (ultra-thin layers, Figure 1) for the TMA+H_2O thermal ALD process with the support of LHAR , contrast SEM and imaging ellipsometry techniques. The merit of using imaging ellipsometer is that beyond visualizing the second front, it also facilitates the measurement of film thickness within the second front region. We checked the process at two different deposition temperatures (125°C and 300°C) and with different combinations of pulsing and purging lengths to investigate the influence of these parameters on the observed secondary growth front. The observation of secondary growth front for both temperatures unambiguously ruled out the deposition temperature influence on the observed feature. To investigate the possible mechanistic reasons for the secondary growth front, we have carried out microkinetic modelling of ALD cycles over a range of combinations of precursor pressures, simulating the situation at various cavity depths. As expected, high pressure of both precursors leads to high growth rates up to the primary growth front. At the lower pressures that are present further into the cavity, the model predicts much lower growth rates, along with an increase in the sticking coefficient of TMA (Figure 2). As the depth of a growth front scales with the square root of the sticking coefficient [1], the low-pressure growth front should therefore be deeper than the high pressure one, which matches the experimental observation. Our results indicate that the formation of the second front results from the presence of multiple reaction mechanisms, which are otherwise challenging to distinguish.

Reference

[1] K. Arts, V. Vandalon, R.L. Puurunen, M. Utriainen, F. Gao, W.M.M. Kessels, H.C.M. Knoops, J. Vac. Sci. Technol. A 37, 030908 (2019).

9:15am **AF1-WeM-6 Helium Ion Microscopy on ALD Thin Films***, Sami Kinnunen,* University of Jyväskylä, Finland*; E. Alakoski, T. Laine,* JAMK University of Applied Sciences, Finland*; T. Sajavaara,* University of Jyväskylä, Finland

Scanning electron microscopy (SEM) is routinely used to image thin nanoscale features such as thin films. Helium ion microscopy (HIM) is in many ways a very similar imaging method with few key differences. In HIM helium ion beam is used to scan the sample and back scattered electrons are detected. In addition to excellent resolution and depth-of-field, charging of insulating samples is easily counteracted with electron flood gun and no extra conductive coating is needed. It is also possible to use neon beam to mill material or fabricate patterns. On the other hand, the minimal generation of x-rays makes elemental analysis more complicated compared to SEM.

In this work we present examples of HIM at the University of Jyväskylä related to ALD and thin film research. For example, imaging insulating cellulose fibers (Fig. 1 a) or packaging materials coated with non-conducting thin films are regularly studied without any special sample preparation. We also show how HIM has been used as a focused ion beam (FIB) tool by changing the incident beam from helium to neon. This can be used, for example, to reveal the cross-section of the ALD film on a substrate (Fig. 1 b). We also show how HIM-based ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) can be used for elemental imaging with high spatial resolution and discuss the limitations of the technique at its current state.

9:30am **AF1-WeM-7 Understanding the Amorphous Structure of Al- and Zn- Doped TiO_2 with an Automated 4D-STEM Analysis Pipeline***, Andreas Werbrouck, N. Paranamana, X. He, M. Young,* University of Missouri-Columbia

Titanium oxide is an ALD staple. It finds uses in microelectronics, (photo) catalysis and lithium-ion-based energy storage. One of the reasons for its attractiveness is the possibility to tune the functional properties by means of the structure: e.g. the conductivity of the material changes by means of doping and/or phase selection through annealing (anatase or rutile).

Amorphous TiO_2 is subject to similar effects. Small concentrations of impurities (e.g. dopants or precursor ligands) may have a large impact on the final structure. Similarly, subtly different structures may arise at the substrate-film or film-vacuum interface. This will affect the functional properties of the films. Due to the difficulty characterizing the nature of the amorphous phase, such differences are easily overlooked. Hence, it is necessary to develop spatially resolved, structural characterization techniques for both crystalline and amorphous materials.

In this work, we report on a 4D-scanning transmission electron microscopy (4D-STEM) investigation of the amorphous structure of undoped and doped TiO_2 as deposited with $TiCl_4$ and water, with $AlMe_3$ and $ZnEt_2$ as precursors for the doping. 4D-STEM measurements allow to investigate and map material structure at the nanoscale in a TEM: 2D diffraction data is available for every recorded pixel and can be combined with co-located Energy-Dispersive X-ray Spectroscopy (EDS) data to match structures and compositions.

The large volume of data and the complexity of diffraction analysis makes manual processing of 4D-STEM data prohibitively slow. To address this, we developed an automated workflow for analyzing 4D-STEM data. This workflow is cast as a Directional Acyclic Graph (DAG). First, the 4D data is split into spatially mapped crystalline and amorphous components. Then, non-local averaging and non-negative matrix factorization distill the amorphous data into a low number of higher-quality pair distribution functions (PDFs). Finally, these can be structurally refined using reverse Monte Carlo (RMC) fitting and molecular dynamics (MD).

This automated approach greatly reduces the amount of time and effort necessary to interpret the data in a meaningful way. Specifically for TiO_2, we clearly observe how even a low level of Zn, Al and Cl impurities profoundly alter the amorphous structure. Through this effort, a better understanding of the as-deposited, amorphous material is gained, which can then serve as a stepping stone to study and engineer more advanced dielectrics, catalysts and electrode interfaces.

9:45am **AF1-WeM-8 Non-Destructive Characterization of ALD Thin Films Using Angle-resolved XPS and Structure Modeling***, K. Artyushkova, N. Biderman,* ***Wolfgang Betz****,* Physical Electronics USA

A powerful tool for surface and interface analysis: X-ray photoelectron spectroscopy (XPS) has long been a trusted technique for analyzing the chemical composition of thin layers and interfaces, offering a non-destructive approach to unlocking valuable information. Angle-resolved XPS (AR-XPS) builds upon this foundation, leveraging the power of tilted measurements to determine the composition and thickness of multilayered films, reaching depths of up to 5-10 nanometers below the surface.

Conventional structure modeling algorithms applied to AR-XPS data rely on the assumption of uniform, discrete thin film growth. This approach presents significant limitations for accurate thickness determination when analyzing films with complex morphologies: pinholes, island growth, and

non-uniform coverage which are particularly observed in atomic layer deposition (ALD) processes.

Structure modeling package *Strata*PHI goes beyond the limitations of conventional ARXPS data modeling for multilayered films. Its fractional coverage mode tackles non-uniform island morphologies typically seen in early ALD stages. This talk highlights *Strata*PHI's capabilities, including layer coverage and accurate thickness even for non-uniform layers.

By employing the microprobe X-ray spot of PHI XPS instruments, capable of analyzing areas ranging from as small as 5 µm in diameter and as large as 1mm x 200 µm, AR-XPS measurements can be used to assess thickness and coverage variations across multiple length scales providing deeper insights into growth mechanisms.

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