ALD Fundamentals
Room Halla Hall - Session AF1-MoA

ALD on 3D Structures

Moderators: Hao Van Bui, Phenikaa University, **Arrelaine Dameron**, Forge Nano

4:00pm **AF1-MoA-11 Continuous Production of Nanocoated Powders**, ***Sébastien Moitzheim***, Powall, Netherlands **INVITED**

Powder-based processes are critical to a wide range of industries, from battery materials to pharmaceuticals. Achieving the desired performance often depends on precise surface modifications.Over the past decade, Powall has been developing a scalable nanocoating technology that combines the atomic-level precision of Atomic Layer Deposition (ALD) with the speed and throughput of Chemical Vapor Deposition (CVD), enabling continuous and cost-effective production.

In this presentation, Dr. Moitzheim (CTO) will share Powall's key learnings on transitioning gas-phase coating methods from lab to pilot-scale and beyond. Specific attention will be paid to how the technology can be adapted to accommodate powders of varying sizes, shapes, and porosities, while still ensuring uniform and high-quality coatings. The talk will also provide an update on the upcoming commercial pilot-scale equipment and outline the path toward large-scale manufacturing. By illustrating the core challenges and advancements in scaling powder nanocoatings, this talk will offer a balanced perspective for researchandindustry.

4:30pm **AF1-MoA-13 Plasma-Enhanced Spatial ALD on 2D and 3D Surface Topologies: The Case of Amorphous and Crystalline TiO_2**, ***Mike van de Poll***, Eindhoven University of Technology, Netherlands*; Jie Shen,* Holst Centre / TNO, Netherlands*; James Hilfiker,* J.A. Woollam Co., Inc.*; Marcel Verheijen, Paul Poodt,* Eindhoven University of Technology, Netherlands*; Fieke van den Bruele,* Holst Centre / TNO, Netherlands*; Erwin Kessels, Bart Macco,* Eindhoven University of Technology, Netherlands

As of late there were two key research questions regarding the conformality of plasma-enhanced spatial ALD (PE-s-ALD): can the technique be used to deposit highly conformal films, and how do the material properties – like crystallinity and composition – of such films change throughout the coated 3D structures? We have recently answered the first question by showing that exceptionally conformal films can be grown by PE-s-ALD with subsecond plasma exposures, thanks to the high radical density in the atmospheric plasma [1]. However, various crystallization and growth effects can influence the film profile and crystallinity, and understanding these effects and their interplay is key.

In this work, we demonstrate the complex growth mechanism of TiO_2 using PE-s-ALD, and study conformality not just in terms of films thickness, but also in terms of film properties. TiO_2 films are deposited both on planar substrates and inside lateral high-aspect-ratio (LHAR) test chips (PillarHall™ by Chipmetrics Ltd). These LHAR structures uniquely allow for spatial material property mapping in trenches using spectroscopic ellipsometry, Raman spectroscopy and X-ray photoelectron spectroscopy. Conditions that result in the anatase phase on a planar surface only partially form this phase inside LHAR structures, with the deepest part of the film being amorphous. This partial crystallization is ascribed to the film thickness inside the LHAR structure gradually dropping below the critical thickness for crystallization. In turn, the partial crystallization is shown to have a significant effect on the resulting thickness profile, due to an enhanced growth per cycle on crystalline surfaces. A framework of the interplay between effects is proposed, offering insights that enable better control of the crystallinity and thickness throughout the entirety of coated surfaces of 3D structures by PE-s-ALD.

Additionally, the recombination probability of O-radicals during this atmospheric-pressure PE-s-ALD process at 200 °C is determined to be 3×10^{-5}, which is similar to low-pressure PE-ALD [2]. This result indicates that differences in conformality between the two types of ALD are not the result of differences in recombination probability, but rather of differences in initial radical density and diffusion behavior.

[1] van de Poll, M. L., Jain, H., Hilfiker, J. N., Utriainen, M., Poodt, P., Kessels, W. M. M., & Macco, B. (2023). *Applied Physics Letters*, *123*(18), 182902.

[2] Arts, K., Deijkers, S., Puurunen, R. L., Kessels, W. M. M., & Knoops, H. C. M. (2021). *Journal of Physical Chemistry C*, *125*(15), 8244–8252.

4:45pm **AF1-MoA-14 Rapid Test for ALD in High Aspect Ratio Spaces Utilizing Thermally Bonded Chips and Hydrazine with Titanium Tetrachloride for TiN Deposition**, *Amy Ross, Dipayan Pal, Dohyun Go, Diego Contreras Mora, Ping-Che Lee,* UC San Diego*; Danish Baig,* Georgia Institute of Technology*; Adrian Alvarez,* RASIRC, USA*; Dan N. Le, Jeffery Spiegelman,* RASIRC*; Muhannad Bakir,* Georgia Institute of Technology*; Andrew Kummel,* UC San Diego*;* ***Walter Hernandez****,* RASIRC

The increasing demand for high-bandwidth memory necessitates the development of devices with 3D structures, such as DRAM. These devices rely on the deposition of conformal, particle-free films with complete coverage in high-aspect-ratio (HAR) spaces. Transmission electron microscopy (TEM) is the standard technique for verifying these parameters, but it is costly, time-intensive, and only inspects a very small area of the surface of interest. This study demonstrates a rapid and non-destructive alternative involving thermally bonded chips that provide HAR spaces for deposition. The chips can be debonded and analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM).ALD titanium nitride (TiN), typically utilized as a 2 nm diffusion barrier between tungsten (or copper) and SiO_2 (or SiCOH) in HAR spaces, was employed using $TiCl_4$ and N_2H_4 precursors, to deposit a 20 nm layer in a thermally bonded chip with a 2000:1 aspect ratio (fig. 1). This is 10x the normal thickness of diffusion barriers to increase sensitivity to particle formation.

A control test was conducted on a clean, thermally bonded sample with no TiN deposition (fig 2). The debonded dies were analyzed as planar samples using AFM, SEM, and energy-dispersive spectroscopy (EDS), confirming no detectable titanium (0% atomic percent) in any region (edge, middle, center). The AFM RMS was measured at 2.06 nm. For TiN deposition, increasing precursor doses 1×, 2×, and 3× normal exposure (1x = 500 ms $TiCl_4$, 2750 ms N_2H_4, 30 sec purge, substrate temperature 475°C) were employed to evaluate penetration depth and particle formation. The RMS roughness values for the top die remained low at 1.92 nm, 1.77 nm, and 1.64 nm, respectively. This indicates no particle formation. Atomic Ti percentages from EDS decreased as the effective aspect ratio increased from 475:1 to 2000:1 aligning with predictions from the Gordon Model [1]. Additionally, the 3x smaller %Ti decreases at the center between the 3× and 2× dose sample further support the model's estimation of precursor penetration. Temperature variations across the sample may have prevented complete surface saturation. The low RMS roughness and absence of large features suggest that CVD particle formation did not occur in the HAR space, consistent with the $TiCl_4$ + N_2H_4 chemistry avoiding $NH_4Cl(s)$ formation [2].

AFM was used to analyze an area of over 111 μm^2, revealing no defects or CVD particles. In comparison, a typical TEM survey covers only 0.004 μm^2. This means SEM/AFM in debonded chiplets examined a region ~30,000x larger than TEM allowing large area determination of particles formation in HAR.

5:00pm **AF1-MoA-15 Enhancing Step Coverage in High-Temperature Ald for Advanced Semiconductor Scaling**, *Seung Hyun Lee, Deok Hyun Kim,* ***Kok Chew Tan****, Sung Gi Kim, Gyun Sang Lee, Jung Hun Lim, Jae Sun Jung,* Soulbrain Co., Ltd., Republic of Korea

As semiconductor technology advances, improvements in performance, power efficiency, and area optimization continue to drive innovation. However, increasing device complexity and higher integration levels have exacerbated step coverage challenges during the deposition of high-k thin films in DRAM capacitors, metal gate insulators, and block oxides in 3D NAND. In particular, achieving uniform thin-film deposition on high-aspect-ratio patterns has become increasingly difficult. Additionally, the application of high-temperature processes to enhance film quality can lead to precursor decomposition, further deteriorating step coverage. To address this issue, this study proposes the use of inhibitor technology as an effective approach to improving step coverage in high-temperature atomic layer deposition (ALD) processes. Our experimental results demonstrate that the inhibitor remains stably adsorbed on the substrate surface under various ALD conditions, effectively mitigating step coverage issues. Notably, this inhibition effect persists even at temperatures above 600°C during the growth of Al_2O_3 thin films. Furthermore, a newly developed hydrocarbon-based inhibitor has been identified as optimal, as it fully decomposes into water and carbon dioxide upon reacting with ALD precursors, leaving no residual impurities in the film.

5:15pm **AF1-MoA-16 ALD as the Solution for Uniform Cu Electroplating in High Aspect Ratio Vias*, Matthew Weimer,*** *Sara Harris,* Forge Nano*; Irina Stateikina,* Centre de Collaboration MiQro Innovation (C2MI), Canada*; Dane Lindblad,* Forge Nano*; Marc Guilmain, Xavier Gaudreau-Miron,* Centre de Collaboration MiQro Innovation (C2MI), Canada*; Arrelaine Dameron,* Forge Nano

Scaling interconnects to increase device density is a critical bottleneck for a range of applications in the 3D and advanced packaging field. Currently, interconnect density is limited by, amongst other things, the ability to produce reliable, low resistivity, Cu vias at high aspect ratios (AR). Some microelectromechanical system (MEMS) applications, where the interconnect in the device layer is defined by the size of the active component, called the proof mass, are restricted in height due to fabrication limitations of high AR interconnects. As a result, some device architectures are inaccessible, limiting the utility of devices, such as high-sensitivity inertial sensors. While some progress has been made, single-side deposition used in blind vias is limited to 8:1 or less. The source of that limitation is the physical vapor deposition (PVD) processes used to apply adhesion and/or nucleation layers required for successful Cu electrochemical deposition (ECD). PVD provides high-quality layers, but those layers are applied in a non-conformal fashion, leading to device failure in non-line-of-site or high AR features, as shown in Figure 1. We have been working on a complete thermal ALD solution at <300 °C consisting of a high-quality SiO_2 dielectric barrier, breakdown voltage >12 MV/cm, a dense TiN Cu diffusion barrier, density ~5.0 g/cm^3, which also functions as a Ru nucleation layer, and low resistivity Ru metal Cu seed layer, resistivity <20 $\mu\Omega\cdot$cm at 20 nm. In this work, we demonstrate successful Cu seed application by depositing this ALD dielectric/diffusion barrier/Cu seed layer stack on Si trenches, where the state-of-the-art PVD solution has multiple failure modes. Successful conformal ECD has been demonstrated with 15-20 nm of Ru in vias with AR from 4:1 to 25:1 and in through glass vias (TGV) with AR from 6:1 to 30:1. Further tests are ongoing with collaborators at the National Institute of Standards and Technology (NIST) to refine Cu ECD conditions and measure via resistivity of Cu ECD in the vias.

5:30pm **AF1-MoA-17 Multi-Scale Model for Optimization of Low-Temperature Al_2O_3 ALD Process Conformality Within High Aspect Ratio Trench*, Ivan Petraš,*** *Yury Shustrov, Andrey Smirnov,* Semiconductor Technology Research d.o.o. Beograd, Serbia

ALD is typically characterized by two main steps with self-limiting reactions on the surface and purging. Each step requires a certain time to ensure complete coverage of the surface by precursor and complete removal of the precursor from the reactor volume during the purging steps. ALD process optimization requires achieving the minimal ALD cycle duration while preserving good conformality within the trench structures over the wafer surface. Optimal process conditions are changed with respect of the trenches pattern, trench surface density and aspect ratio. Therefore, the process adjustment on the blanket wafers becomes inefficient, while the adjustment cost with the patterned wafers is typically high. In this sense, multi-scale models with the coupled reactor-scale and feature-scale simulations can be applied for reducing of process development costs. Focus of this work is aimed at the improvement of low-temperature Al2O3 ALD performance with consideration of patterned wafers through adjustment steps duration and operating conditions. An integrated modeling approach was developed with self-consistent coupling of modeling tasks on different scales. The reactor-scale model of TMA delivery, oxidation by H2O and purging includes unsteady mass transport with surface chemical reactions. The trench-scale model includes tracing TMA and H2O species as well as products of surface chemical reactions.It is demonstrated that increasing of trench aspect ratio leads to remarkably longer time for achieving of ALD conformality on patterned wafer during both TMA delivery and oxidation steps. The increase of precursor impulse duration results in the reducing of time required for full coverage, but simultaneously it increases the needed time for purge step before introduction of the next precursor. As the result the increasing the precursor pulse duration for better conformality within the trench may lead to requirements of longer time for ALD cycle and thus decrease the throughput of the process. Pressure effect on the trench coverage time demonstrates different trends with the aspect ratio change during TMA and H2O steps. At lower aspect ratio of 20 the pressure decrease leads to faster trench coverage, while for high aspect ratio of about 100 there is the non-monotonic behaviour of coverage speed with pressure change. It is demonstrated that a detailed consideration of low temperature oxidation mechanism is important to correctly describe the oxygen incorporation into the film and resulting ALD conformality. Effect of temperature and H2O purge step duration on the resulting film stoichiometry are discussed.

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