

## Area Selective ALD

### Room Tamna Hall A - Session AS2-WeM

#### Area Selective Deposition III

**Moderators:** Rick Chen, Merck KGaA, Darmstadt, John Conley, Oregon State University

10:45am **AS2-WeM-12 Industrial ALD/ASD Perspectives: Atomic Level Process Control for Semiconductor Devices**, HanJin Lim, Samsung Electronics, Republic of Korea **INVITED**

As the semiconductor devices are highly integrated and refined to feature sizes of 10 nm or less, the thickness of the functional films that affect the electrical properties of the device is also thinned to 5 nm or less. Since the role of the interface becomes dominant in such a functional thin film, engineering techniques using various interfacial layers for electrical properties are being introduced. On the other hand, in order to implement such a thin film in a 3D semiconductor structure, ALD technology is essential, and various processes and interfacial layer technology introduction cases are to be examined for phase stabilization and interface control of atomic level film quality. In addition, in order to realize high-quality and uniform film quality in a complex 3D structure, we will look at examples of innovation in ALD precursors and facility technologies and advancement of process technologies, and finally, we will look at cases of improvement in semiconductor device characteristics using selective deposition technology.

11:15am **AS2-WeM-14 Area-Selective Deposition for Dielectric Films on Metal Substrates: Coupon to Full Wafer**, Rachel Nye de Castro, Paul Lemaire, Alexander Fox, Joel Smith, Nupur Bihari, Bill Nunn, Kevin McLaughlin, Dennis Hausmann, LAM Research

Area-selective deposition (ASD) has potential to reduce reliance on costly lithography steps and improve shorting margins for small pitch sizes. ASD has been successfully demonstrated for many material sets, notably dielectric on dielectric (DoD) for fully self-aligned vias,<sup>1</sup> yet the demand for thicker films and new materials continues to grow to enable advanced applications. Selectively depositing a film on a surface of a different type, e.g. a dielectric film on a metal substrate, is inherently more challenging because after the first few cycles of deposition, both the growth and non-growth surfaces are the same type (dielectric in this example), resulting in similar reactivity towards ALD precursors. This work discusses the development of selective dielectric on metal (DoM) deposition from coupon-scale to full wafer patterns.

We utilize inhibitor molecules to selectively block deposition on our desired non-growth surface (dielectric in this case). Numerous inhibitors are screened on both dielectric (SiO<sub>2</sub>, SiON, SiOC, etc) and metal (W, Co, Cu, Ru, etc) surfaces using water contact angle (WCA) measurements to characterize hydrophobicity after selective inhibitor adsorption. Inhibitors with the best WCA contrast between dielectric and metal are then evaluated for blocking performance using AlO<sub>x</sub> ALD. Ellipsometry, mass, and x-ray reflectivity measurements demonstrate several nm of AlO<sub>x</sub> deposition on metal surfaces without any selectivity loss on dielectric. Further verification from TEM and EELS elemental analysis confirm that this selectivity is extended to patterned coupons and full wafers. We demonstrate selective AlO<sub>x</sub> on patterned wafers with excellent selectivity (EELS, top-down SEM), which is also extended to other deposited films (e.g. SiN, MoN). These inhibitors are compatible with high volume manufacturing requirements, 3D features, and a wide range of temperatures that accommodates low thermal budget materials as well as high temperature ALD processes. This selective DoM process enables applications such as selective hard masks and etch stop layers and improved shorting margins.

#### References

Parsons, G. N.; Clark, R. D. *Chem. Mater.* **2020**, *32*, 4920-4953.

11:30am **AS2-WeM-15 Redox-coupled Inherently Selective Atomic Layer Deposition of SiO<sub>2</sub> on SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> for 3D NAND structure**, Kun Cao, Zilian Qi, Eryan Gu, Rong Chen, Huazhong University of Science and Technology, China

Area-selective atomic layer deposition (AS-ALD) provides a promising approach for bottom-up fabrication by enabling atomic-level control over material growth in pre-defined patterns, particularly on complex 3D architectures. In this study, a novel strategy is proposed that combines surface-state modulation via alcohols pre-treatment with oxygen partial

pressure optimization to enhance selectivity between SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> surfaces. Methanol pre-treatment maintains the amination of Si<sub>3</sub>N<sub>4</sub> surfaces, effectively delaying nucleation in non-growth regions, while controlling oxygen partial pressures prevent undesired oxidation of amines to hydroxyl groups. Di(isopropylamino)silane (DIPAS) is employed as a selective SiO<sub>2</sub> precursor, demonstrating inherent selectivity without additional surface inhibitors. The inclusion of dynamic precursors pulses in the ALD process further improved precursor transport and reaction uniformity in high-aspect-ratio 3D NAND structures. This approach achieved ~3 nm thick SiO<sub>2</sub> films on SiO<sub>2</sub> surfaces, with minimal deposition on Si<sub>3</sub>N<sub>4</sub> surfaces. Uniform deposition across the top and bottom layers of high aspect ratio 3D structures is demonstrated. This approach combines methodology of surface-state engineering and dynamic precursor pulsing highlights a robust method for expanding AS-ALD applications in complex 3D nanoelectronics.

11:45am **AS2-WeM-16 Area-selective Atomic Layer Deposition of Ruthenium via Plasma Surface Modification**, In-Hwan Baek, Dahui Jeon, Inha university, Republic of Korea

As semiconductor devices continue to scale down and increase in complexity, achieving both high performance and reliability has become increasingly critical. Ruthenium (Ru) has emerged as a key material for next-generation interconnects and electrode applications due to its low resistivity (~7.1 μΩ·cm), high work function (~4.7 eV), and excellent chemical stability. To fully utilize these properties, area-selective atomic layer deposition (AS-ALD) is essential for enabling Ru deposition exclusively in growth regions while inhibiting it in non-growth areas. This bottom-up patterning approach mitigates edge placement error (EPE) and enhances overall process yield.

Conventional AS-ALD techniques using self-assembled monolayers (SAMs) as surface inhibitors are inherently limited by their low thermal stability, leading to selectivity degradation over multiple cycles. As the deposition process proceeds, SAM desorption or decomposition leads to unwanted Ru nucleation in non-growth regions, compromising the selectivity of the process. Furthermore, achieving uniform SAM coverage in high-aspect-ratio structures poses additional challenges.

To overcome these limitations, we developed an atmospheric-pressure X plasma surface modification process, which introduces hydrophobic functional groups that effectively suppress Ru nucleation in non-growth areas while maintaining stability throughout multiple ALD cycles. This method demonstrated infinite selectivity, with no Ru deposition detected in non-growth regions even after 200 ALD cycles, while achieving over 30 nm of Ru film growth in targeted areas—exceeding the selectivity performance of conventional AS-ALD approaches.

Additionally, we established a substrate-dependent X plasma effect, demonstrating selective removal of hydrophobic X functional groups based on surface chemistry, which influenced Ru nucleation behavior. Furthermore, we verified that post-deposition atmospheric O<sub>2</sub> plasma treatment effectively eliminates residual X inhibitors from non-growth areas without compromising Ru film integrity in growth regions. These findings highlight plasma-assisted AS-ALD as a scalable, highly selective approach for advanced semiconductor integration.

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