

## ALD for Manufacturing

### Room Samda Hall - Session AM-WeA

#### ALD Equipment

**Moderators:** Eun-Hyoung Cho, 2D Device TU(SAIT)/Samsung Electronics, Woo Jae Lee, Pukyong National University, Tae Wook Nam, Sejong University

#### 1:30pm AM-WeA-1 Spatial Atomic Layer Deposition of Cu-Based Thin Films, David Muñoz-Rojas, CNRS, France **INVITED**

Spatial Atomic Layer Deposition (SALD) is an emerging variant of ALD that enables rapid processing, even at atmospheric pressure, while retaining the key advantages of ALD: precise nanometer-scale thickness control, high-quality films at low temperatures, and exceptional conformality. These features make SALD particularly well-suited for high-throughput, cost-effective applications, such as next-generation photovoltaics, LEDs, and packaging.

A key strength of SALD, especially when utilizing close-proximity deposition heads, lies in its versatility. The design of these deposition heads can be easily customized, and since the process takes place in open air, no deposition chamber is required, further simplifying scalability.

To fully leverage the benefits of SALD, however, new processes must be developed to deposit functional materials with optimized properties using mild conditions and stable precursors. In this talk, I will introduce our close-proximity SALD approach and highlight our recent work in developing innovative SALD processes. Specifically, I will present a novel SALD method for depositing Cu<sub>2</sub>O thin films with record-high transport properties, achieved despite low-temperature processing. I will also explore the critical role of precursors and process conditions in determining the final film properties. Lastly, I will demonstrate that, even in an open-air environment, it is possible to selectively deposit Cu, Cu<sub>2</sub>O, or CuO from the same precursor simply by adjusting the coreactant.

#### References

Open-Air Printing of Cu<sub>2</sub>O Thin Films with High Hole Mobility for Semitransparent Solar Harvesters

A. Sekkat, et al. *Commun Mater* 2, 78 (2021)

Chemical deposition of Cu<sub>2</sub>O films with ultra-low resistivity: Correlation with the defect landscape.

A. Sekkat, et al. *Nature Communications*, 2022, 13, Article number: 5322

Open-Air, Low-Temperature Deposition of Phase Pure Cu<sub>2</sub>O Thin Films as Efficient Hole-Transporting Layers for Silicon Heterojunction Solar Cells

V. S. Nguyen†, A. Sekkat†, et al. *J. Mater. Chem. A*, 2021, 9, 15968-15974.

Selective spatial atomic layer deposition of Cu, Cu<sub>2</sub>O and CuO thin films in the open air: reality or fiction?

A. Sekkat, et al. *Materials Today Chemistry*, 2023,29, 101431.

Nanocomposites based on Cu<sub>2</sub>O coated silver nanowire networks for high-performance oxygen evolution reaction

S. Battiato, et al. *Nanoscale Advances*, 2024, 6, 4426-4433.

Assessing the Potential of Non-pyrophoric Zn(DMP)<sub>2</sub> for the Fast Deposition of ZnO Functional Coatings by Spatial Atomic Layer Deposition

L. Johnston, et al. *RSC Applied Interfaces*, 2024, 1, 1371-1381

#### 2:00pm AM-WeA-3 Spatial ALD Deposited Functional Layers for Large-Area Inverted Perovskite Solar Modules, Xuwei Jiang, Fan Yang, Bin Shan, Rong Chen, Huazhong University of Science and Technology, China

Perovskite solar cells (PSCs) are a promising candidate for large-scale commercialization, with efficiency and scalability as key factors. However, fabrication of large-area functional thin films including electron transport layers (ETLs), hole transport layers (HTLs) as well transparent conductive electrode, becomes one of the biggest obstacles for the commercial PSCs applications. This study explores low temperature SALD deposited SnO<sub>2</sub> ETL and aluminum-doped zinc oxide (AZO) as transparent conductive oxide electrodes to improve the performance of PSCs modules. By controlling oxygen vacancies through precursor reactivity, we achieved a high mobility of 19.4 cm<sup>2</sup>/V·s in SnO<sub>2</sub> ETL (deposited at 100 °C) and ultra low sheet resistance to 3.6 Ω/sq for AZO electrode, surpassing commercial FTO (8 Ω/sq). Additionally, textured AZO electrodes, exhibited excellent optical properties with a haze of over 55% and an average transmittance of approximately 90%. Due to the advantages of SALD, the thin films

demonstrated good uniformity with only 2.8% nonuniformity in film thickness and 4.6% in sheet resistance over a 400 cm<sup>2</sup> area. For the 400 cm<sup>2</sup> PSMs with AZO electrodes achieve a PCE of 20.5% and retain 87% of their initial efficiency after 600 hours of continuous illumination. This exceptional performance stems from the excellent uniformity and mobility of the SALD-deposited SnO<sub>2</sub> ETL and AZO electrode, highlighting the potential of SALD in future PSM fabrication.

#### References

1. Scalable Deposition of SnO<sub>2</sub> ETL via SALD for Large-Area Inverted Perovskite Solar Cells. Xuwei Jiang, Bin Shan, Geng Ma, Yan Xu, Xing Yang, Wenbin Zhou, Chenhui Li, Fan Yang, and Rong Chen, *Chem. Eng. J. Accepted*.

#### 2:15pm AM-WeA-4 Atomic Layer Deposition on Highly Cohesive Granular Material in Fluidized Beds, Rens Kamphorst, Delft University of Technology, Netherlands; Kaiqiao Wu, Delft University of Technology, China; Saeed Saedy, Gabrie M.H. Meesters, J. Ruud van Ommen, Delft University of Technology, Netherlands

Atomic layer deposition (ALD) on granular materials is gaining increasing attention due to its potential applications in pharmaceuticals, nano-catalysts, and colloidal stabilization. Powders with smaller particle sizes have higher specific surface areas, which can be utilized, however, they pose significant challenges for processing, especially when particle sizes are <30µm. At these scales, van der Waals forces dominate making particles cohesive. In conventional fluidized beds, ALD is challenged by precursor gas escaping via cracks in the powder bed, having little interaction with the particles. Furthermore, particle clusters appear frequently, resulting in parts of individual particles being inaccessible to be coated, leading to non-uniform deposition. These complications necessitate dedicated systems that can overcome the inherent cohesiveness of such powders.

In our work, we set out to coat cohesive particles in an ALD fluidized bed reactor. We employed X-ray imaging to evaluate methods for improving fluidization of cohesive powders, including mechanical vibration, pulsed flow, and mechanical agitation. These methods are designed to break up structures within the powder, improving gas-solid interaction.

Our findings demonstrate that assistance methods initiate smooth fluidization, significantly enhancing gas-solid contact. We visualize the dynamics within powder beds subjected to various assistance methods and propose scalable methods to fluidize cohesive powders in order to perform ALD. We also show successful deposition of SiO<sub>2</sub> layers on otherwise un-fluidizable particles. These results open pathways for functionalizing fine powders for advanced technological applications.

#### 2:30pm AM-WeA-5 High Deposition Rate TiO PEALD Process for Semiconductor Industry, Sungbae Kim, Yeahyun Gu, Hyunchul Kim, Hyungjoo Shin, ASM, Republic of Korea

TiO thin films are increasingly used in the semiconductor industry due to their excellent physical and chemical properties. Due to their high etching selectivity for the Si base materials and pattern fidelity, they have been mainly used for patterning applications such as hard-mask and spacers. Recently, however, due to the material's unique optical property (High Refractive Index (R.I.) value >2.3 at 633nm), the application area has been expanded to others such as ARL (Anti-Reflection Layer) and CIS (CMOS Image Sensor) Meta-lens. As such applications often require a thicker material than patterning films, a higher deposition rate is accordingly desirable for commercially viable productivity.

In this paper, a new process sequence was developed to increase the deposition rate while keeping the most of benefits of PEALD including film quality, uniformity, and gap fill capability. The thin film properties were characterized and compared with those of the conventional ALD process. TDMAT was used as the Ti precursor. O<sub>2</sub> plasma was used as the reactant to grow TiO. 27.12MHz-rf source was used to generate a CCP in a commercial PEALD chamber by ASM (QCM TiO XS).

In the case of conventional ALD, there is a limitation in terms of the deposition rate even with the increasing supply of precursor due to the nature of self-limiting reaction phenomenon in PEALD. To overcome this self-limiting reaction, a low-power pulsed-plasma CVD step was introduced in a typical PEALD process cycle. (Figure1.) The new process sequence promotes the film growth by balancing the conformal deposition and the surface treatment. By this means, the new deposition rate increased to 0.94Å/sec by nearly three times compared to conventional ALD (0.34Å/sec). The results of the film deposited on a 12-inch bare Si wafer by the new process shows both uniformity and R.I. are at similar levels as the ones with conventional slow PEALD. In addition, we confirmed the step coverage is

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more than 80% in the pattern of open CD 90nm with aspect ratio of 3. XPS analysis also shows that the impurity concentrations of 'C' and 'N' were as low as below 2%, which is comparable to conventional PEALD process.

The high deposition rate TiO PEALD process is expected to be applicable to any new emerging applications which requires TiO's PEALD quality yet with higher deposition rate. The ASM's hardware technology enables this new process sequence for a novel PEALD.

**2:45pm AM-WeA-6 Advancing Atomic Layer Processing for Next Generation Devices: Atlant 3d'S Direct Atomic Layer Processing (Dalp™), Mira Baraket, ATLANT 3D Nanosystems, Denmark**

As the demand for miniaturized and complex devices accelerates across industries, innovative and precise atomic layer advanced manufacturing techniques have become critical. ATLANT 3D's proprietary Direct Atomic Layer Processing (DALP™) technology is redefining thin-film processing by enabling spatially localized, atomically precise material growth with unmatched flexibility. Building upon Atomic Layer Deposition, DALP™ confines gas flows to a micrometer-scale area using advanced microreactors, enabling deposition of diverse materials on complex geometries and substrates with exceptional thickness control and conformality on complex structures.

DALP™ technology tackles key challenges in accelerating innovation within thin-film manufacturing. It enables rapid prototyping by allowing localized, multi-thickness depositions of diverse materials on a single wafer, significantly cutting prototyping timelines from months to hours compared to conventional methods. These capabilities have been demonstrated across diverse applications, including optics and photonics, MEMS, RF electronics, emerging memory technologies, advanced packaging, and energy storage.

This talk will explore ATLANT 3D's advancements in DALP™ technology, focusing on expanded material compatibility, enhanced resolution, and new opportunities it creates for thin-film processing. We will demonstrate how DALP™ technology drives innovation by enabling the fabrication of complete, functional devices. Through case studies, we will highlight how our advanced processing technique have been used to produce components and electronic devices. These examples illustrate how ATLANT 3D's platform not only improves material deposition processes but also revolutionizes prototyping and manufacturing, empowering industries to achieve faster and more efficient innovation.

**4:45pm AM-WeA-14 Closing Remarks and Awards in Tamna Hall A,**

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