ALD for Manufacturing
Room Samda Hall AB - Session AM1-WeA

ALD Equipment I

Moderators: Eun-Hyoung Cho, 2D Device TU(SAIT)/Samsung Electronics, **Woo Jae Lee**, KNU

1:30pm **AM1-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_2O 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_2O, or CuO from the same precursor simply by adjusting the coreactant.

References

Open-Air Printing of Cu_2O Thin Films with High Hole Mobility for Semitransparent Solar Harvesters

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

Open-Air, Low-Temperature Deposition of Phase Pure Cu_2O 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_2O and CuO thin films in the open air: reality or fiction?

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Nanocomposites based on Cu_2O 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 $Zn(DMP)_2$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 **AM1-WeA-3 Visualization of Precursor Transport in Vapor Deposition Systems: Measurements and Simulations*, James Maslar,*** *Vladimir Khromchenko, Berc Kalanyan,* NIST-Gaithersburg

Advanced models for semiconductor fabrication unit processes are needed for improved process control, defect reduction, and ultimately yield improvement. Development of such models is limited by a general lack of non-proprietary process data. The goal of this work is to aid in vapor deposition process model development by 1) generating measurement data sets and 2) evaluating the utility of these data sets by using them to validate simulations of precursor flow in our ALD chambers. Central to achieving this goal is absorption imaging of precursor flow as a function of process conditions, e.g., gas flow rate, chamber pressure, and temperature. Two precursors were selected for investigation: molybdenum pentachloride ($MoCl_5$) and tetrakis(dimethylamido)titanium (TDMAT). $MoCl_5$ flow was visualized at about 100 images per second in the ultraviolet-visible spectral region using a 7.1-megapixel complementary metal oxide semiconductor camera and a light emitting diode source. TDMAT flow was visualized at about 30 images per second in the mid-infrared spectral region using an uncooled microbolometer thermal imaging camera and a blackbody source. Simulations of flow in this chamber were performed using a commercial computational fluid dynamics (CFD) package. CFD simulations of low-volatility precursors in a carrier gas are simplified since the precursor is dilute and the gas properties are that of the carrier gas, properties that are well known for typical deposition conditions. Simulations were validated using the time-dependent, pathlength-integrated precursor concentration obtained from the absorption imaging measurements and the time-dependent total pressure measured at selected locations in the deposition system. In this talk, aspects of both the measurements and simulations will be discussed, including the choice of parameters included in the data set.

2:15pm **AM1-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 $<30\mu m$. 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_2 layers on otherwise un-fluidizable particles. These results open pathways for functionalizing fine powders for advanced technological applications.

2:30pm **AM1-WeA-5 From the Research Lab to the Fab: Comparison of Vapor Generation by Bubbler and Direct Liquid Injection Vapor Delivery Systems*, David Curran,*** 5910 Rice Creek Parkway Suite 300

As the semiconductor industry is moving to smaller nodes, the need for high-quality and high-throughput vapor delivery is paramount. As the geometry and structures of the depositions evolve, research institutions and chemical manufacturers are developing new precursors offering superior reaction mechanisms for selective surface depositions and other difficult reactions. Initial testing of these precursors in chemical vapor deposition or atomic layer deposition processes are typically conducted by supplying the vapor by means of a bubbler or a flow over vessel. Bubblers in conjunction with a downstream ALD valve can be a straightforward solution; however mass delivery accuracy, adjustability and stability are known issues, which can create thin film irregularity and wafer-to-wafer variability. Additionally, if precursors are thermally sensitive, there can be issues with the liquid decaying in the heated ampoule over time leading to long deposition times and/or wasted material. To meet the industry needs, a solution is needed to improve vapor delivery to scale up from development to production.

Direct liquid injection (DLI) vaporizing systems present an attractive solution to the scale-up problem. DLI systems allow the throughput of the vapor delivery system to be increased by generating nanometer to micron sized droplets of the precursors, improving the heat transfer to the liquid. Coupled with a liquid flow controller, DLI systems can provide fast, high-throughput, consistent, known concentrations of vapor to deposition chambers.

The work presented in this presentation will directly compare the vapor concentration and quality delivered by a bubbler and a DLI vaporizer for several difficult to vaporize precursors. To compare the delivery systems, a method using Fourier Transform Infrared (FTIR) spectroscopy to conduct real-time measurement of vapor concentration and droplet content of the vapor stream will be employed. This presentation will briefly detail hardware and experimental setup used, key control criteria, and advantages and disadvantages will be discussed.

2:45pm **AM1-WeA-6 Advancing Fast Spatial Atomic Layer Deposition: Optimizing Precursor Control and Atmospheric Effects for Functional Oxide Thin Films***, **Viet Huong Nguyen,*** Faculty of Materials Science and Engineering, Phenikaa University, Hanoi 12116, Viet Nam., Viet Nam

Spatial atomic layer deposition (SALD) has emerged as a powerful technique to achieve high deposition rates while maintaining the atomic precision of conventional ALD. However, challenges persist in controlling unwanted chemical vapor deposition (CVD) contributions and optimizing process parameters for large-scale applications. In this work, a comprehensive study on enhancing control in SALD by tuning precursor diffusion, injection head geometry, and deposition conditions will be presented. Using a combination of experimental data and computational modeling, we elucidate the critical role of precursor exposure and deposition gap on growth kinetics, leveraging insights from ZnO and SnO_2 thin films.[1] A refined injection head design is proposed to mitigate CVD-related issues while maximizing throughput. Furthermore, we investigate the impact of atmospheric pressure on the electrical properties of metal oxide semiconductors,[2–4] and suggest a few strategies to enhance control over growth and functionality for optoelectronic and energy applications.[5]

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3:00pm **AM1-WeA-7 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 requires 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. O2 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 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.

3:15pm **AM1-WeA-8 Spatial ALD Deposited Functional Layers for Large-Area Inverted Perovskite Solar Modules***, **Xuewei Jiang,*** Huazhong University of Science and Technology, China*; Fan Yang,* Luoyu Road 1037, Wuhan, China*; 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_2 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 $cm^2/V{\cdot}s$ in SnO_2 ETL (deposited at 100 ℃) 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^2 area. For the 400 cm^2 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_2 ETL and AZO elelctrode, highlighting the potential of SALD in future PSM fabrication.

References

1. Scalable Deposition of SnO_2 ETL via SALD for Large-Area Inverted Perovskite Solar Cells. Xuewei Jiang, Bin Shan, Geng Ma, Yan Xu, Xing Yang, Wenbin Zhou, Chenhui Li, Fan Yang, and Rong Chen*, Chem. Eng. J. Accepted*.

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