ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-WeA

Computational ALD II

Moderator: Dr. Tania Sandoval, Technical University Federico Santa Maria

4:00pm **AF2-WeA-11 Revealing Process-Structure Relationships for ALD Amorphous Oxide Semiconductors with XANES and First-Principles Modeling**, ***Orlando Trejo,*** Applied Materials; *T. Cho,* University of Michigan, Ann Arbor; *S. Sainio,* University of Oulu, Finland; *N. Dasgupta,* University of Michigan, Ann Arbor

Amorphous oxide semiconductors (AOS) lack the long-range order characteristic of crystalline materials but possess short-range order that gives rise to a vast parameter space to design and optimize their properties. To accelerate efforts to control their functional properties and optimize device performance, an increased fundamental understanding of the complex process−structure−property relationships of AOS is needed. Recent research efforts have provided an initial framework to understand how short-range order in AOS determine their properties. The structure and interconnection of the metal-oxygen (M-O) polyhedra in AOS depend on the material system (i.e., the composition and types of elements) and the synthesis conditions (e.g., solution, physical or chemical vapor deposition). Given its atomic-level synthesis control and technological relevance, ALD chemistry facilitates and encourages a systematic structural analysis of AOS that are material and process specific.

In our previous work, we optimized the performance of amorphous ALD zinc tin oxide (ZTO) thin-film transistors by turning the Zn-to-Sn ratio and annealing temperature.[1] However, prior work has not been able to fully uncover the mechanistic origins of the differences in performance among samples. To address this knowledge gap, here we leverage ALD's capability to finely tune the composition of ZTO films along with systematic annealing to reveal how cation composition and annealing temperature influence the geometric and electronic structure in an AOS.[2] The ZTO films are characterized with XRD, XPS, and synchrotron x-ray absorption near-edge spectroscopy (XANES) measurements of the O K-edge, Sn M-edge, and Zn L-edge. The XANES spectra are analyzed with ab initio and nonlinear statistical modeling. The resulting multimodal analysis of ALD ZTO reveals how process conditions give rise to gradual or abrupt changes in the coordination environment of the Zn−O and Sn−O polyhedra, which in turn translate into changes in the relative contribution of the Zn and Sn s orbitals to the density of states near the conduction band minimum. Thus, this multimodal X-ray analysis and modeling framework can be applied to understand the process-structure relationships needed to optimize AOS performance in devices.

(1) Allemang, C. R.; Cho, T. H.; Trejo, O.; Ravan, S.; Rodríguez, R. E.; Dasgupta, N. P.; Peterson, R. L., *Adv. Elec. Mater.* **2020**, *6*, 2000195.

(2) Trejo, O.; Cho, T. H.; Sainio, S.; Dasgupta, N. P., *J. Phys. Chem. C* **2023**, *127*, 338

4:15pm **AF2-WeA-12 Machine-Learning Aided Understanding of ALD Processes**, *A. Arunachalam,* University of Texas at Dallas; ***S. Novia Berriel,*** *U. Kumar,* University of Central Florida; *S. Das,* University of Texas at Dallas; *S. Seal,* University of Central Florida; *K. Basu,* University of Texas at Dallas; *P. Banerjee,* University of Central Florida

ALD processes are controlled via an array of hardware-based, independent process parameters. Typically, 'recipes' are built that enable these parameters to be set to specific values during an ALD process. Example parameters include chuck and chamber temperatures, line and precursor temperatures, gas flow rates, etc. While each of these play an important role in the growth rate and final thickness of an ALD film, there is currently no measure of the magnitude of their impact on the film thickness and quality. Further, there is no way to predict film thickness purely based on process parameters without running numerous experiments to get an estimated growth rate. We propose the use of machine learning (ML) approaches to generate 'feature importance maps' that graphically depict the impact of these parameters in determining and predicting film thickness.

Our ML method begins with a set of 78 process parameters recorded from an ALD process from a Veeco® Fiji Gen2 ALD system for a CeO_2 film. The ALD process has been described in detail elsewhere[1]. A random forest ML algorithm then identifies the top-ten 'critical' independent process parameters that affect film thickness at a given deposition temperature. These include a list of heater zones around the reaction chamber, line pressure of the precursor delivery line, etc. A temperature dependent (from 185 ^oC – 320 ^oC) series is then generated. The model is able to predict with up to 99.99% accuracy the time variation of thickness during the growth, verified via in situ spectroscopic ellipsometry. Our talk will include detailed considerations in generating the ML model, as well as results for a range of process temperatures for CeO_2 ALD.

[1] U. Kumar, C. Feit, S. N. Berriel, A. Arunachalam, T. S. Sakthivel, K. Basu, P. Banerjee and S. Seal, Journal of Vacuum Science & Technology A 39, 060405 (2021).

4:30pm **AF2-WeA-13 Digital Twin and Experimental Platform for AI-Driven Optimization of ALD Processes**, ***Angel Yanguas-Gil,*** *N. Paulson, J. Elam,* Argonne National Laboratory

Atomic layer deposition is an ideal platform for exploring AI-driven optimization and discovery: first, ALD's step-by-step nature defines a natural design space where a growth is defined by sequences of cycles, each of which driven by their own timings; Second, ALD tools already come with the required control software and hardware to integrate with AI engines. Finally, its integration into cluster tools with automatic wafer handling systems in microelectronics opens up the possibility of fully automatic growth-characterization-decision cycles to develop novel materials.

In this work we describe an experimental setup for AI-driven process optimization as well as a digital twin for the development and validation of novel algorithms for self-driving labs. Building on prior research where we used simulated quartz crystal microbalance data, here we expand the range of techniques to incorporate optimization based on in-situ spectroscopic ellipsometry. In addition to algorithms to optimize the dose and purge times of single processes, we have also explored algorithms to find optimal sequences of ALD cycles for binary and ternary compounds based on target optical properties.

From an experimental perspective, we have demonstrated the optimization of ALD processes based on in-situ techniques. While the results are demonstrated in a specific cross-flow reactor, the methodology and algorithms developed can be easily adapted to other reactor configurations and characterization techniques.

This research has been supported through Argonne's Laboratory Directed Research and Development program.

[1] Noah H. Paulson, Angel Yanguas-Gil, Osama Y. Abuomar, and Jeffrey W. Elam, ACS Applied Materials & Interfaces 2021 13 (14), 17022-17033. DOI: 10.1021/acsami.1c00649

[2] Angel Yanguas-Gil and Jeffrey W. Elam, Machine learning and atomic layer deposition: Predicting saturation times from reactor growth profiles using artificial neural networks, Journal of Vacuum Science & Technology A 40, 062408 (2022) https://doi.org/10.1116/6.0001973

4:45pm **AF2-WeA-14 Closing Remarks in Grand Ballroom H-K**,

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