Tutorial Session (ALL INVITED SESSION)
Room Live - Session TS1-SuM

ALD/ALE Tutorial Session

Moderators: Prof. Seán Barry, Carleton University, Canada, Dr. Scott Clendenning, Intel Corporation

10:00am **TS1-SuM-1 Tutorial Opening Remarks & Welcome*, Seán Barry,*** Carleton University, Canada

Welcome to the ALD/ALE 2021 Tutorials! We hope you will enjoy the Session and the Virtual Meeting this week!

10:05am **TS1-SuM-2 ALE and ALD: Two Biotopes of a Kind in Atomic-Scale Processing*, Fred Roozeboom,*** Eindhoven University of Technology, TNO-Holst Centre, Netherlands **INVITED**

The IRDS 2017 Roadmap catches the scaling challenges faced by the semiconductor industry in the upcoming decades by the overall term "3D Power Scaling". In the past scaling era superior material properties and critical dimensions nearing single-digit nanometer values could still be realized by cost-effective technology solutions. As we approach the 3^{rd} scaling era, increased complexity and cost of device fabrication can result in decreased returns for IC manufacturers. Ever more complex device architectures that are fully integrated into vertical intra- and inter-chip concepts require extreme edge placement accuracy, layer conformality and shape fidelity in all processing steps (deposition, lithography, etching).

In state-of-the-art semiconductor processing we witness an ever-progressing hybridization of individual ALD and ALE process steps into 'dep-etch' *supercycling* modes carried out in a single flowchart and a single reactor design, thereby challenging even EUV lithography. This rapid merger finds its grass roots in the close resemblance of the two techniques in terms of cyclic sequential processing, self-limiting surface chemistry and repeated etching or removal of (sub-) monolayers of material. For both ALE and ALD these factors allow for similar process windows that depend on the substrate surface temperature or the kinetic energy of reactants.

In this tutorial more parallels of ALE will be drawn with its more mature and better understood ALD counterpart. Starting with a technical-historical review of dry and reactive ion etching, the key characteristics of ALE will be discussed: the simplest ALE process is composed of two alternating steps, *i.e.* surface modification and (quasi-)monolayer removal. Next, the classification into 1) isotropic (thermal and radical-enhanced) ALE and 2) anisotropic (directional and ion-enhanced) ALE will be treated along the role played by energetic species (radicals, ions in a plasma) in one or two steps with the ions yielding anisotropic profiles (used in FinFET logic and 3D NAND memory), and neutrals and radicals yielding isotropic profiles (used to etch horizontal nanowires in GAA-FETs). Another parallel aspect that may be discussed is the need for (maskless) material-selective processing in both ALE and ALD.

In short, we will identify the similarities and differences between the two process concepts with the aim of bringing common practical insights and recommendations.

(1) The International Roadmap for Devices and Systems: 2017: More Moore; 2017.

10:55am **TS1-SuM-12 Fundamentals of Atomic Layer Deposition: An Introduction ("ALD 101")*, Riikka Puurunen,*** Aalto University, School of Chemical Engineering, Finland **INVITED**

Atomic layer deposition (ALD) has become of global importance as a processing technology for example in semiconductor device fabrication, and its application areas are continuously expanding. The significance of ALD was highlighted e.g. by the recent (2018) Millennium Technology Prize. Tens of companies are offering ALD tools, and thousands of people are involved in ALD R&D globally. A continuous need exists to educate new people on the fundamentals of ALD.

While ALD for manufacturing may be regarded mature, as a scientific field, ALD—in the author's view—is developing. For example, understanding of the early history of ALD is evolving, related to the two independent inventions of ALD under the names Atomic Layer Epitaxy in the 1970s and Molecular Layering in the 1960s [1-4]. Also, significantly varying views exist in the field related to the description and meaningfulness of even some core ALD concepts [5].

The purpose of this invited "ALD 101" tutorial is to familiarize a newcomer with fundamentals of ALD. The presentation largely follows the organization of a recent encyclopedia chapter on ALD [6]. Surface chemistry concepts will be introduced, such as ideal ALD from repeated, separate self-terminating (saturating and irreversible) reactions; growth per cycle in ALD; various monolayer concepts relevant to ALD; typical classes of surface reaction mechanisms and saturation-determining factors; growth modes; and ways to describe growth kinetics. Concepts, where differing views exist in the field and which thus need special attention, are pointed out. Typical deviations from the presented ideality are discussed.

For continuous education, a collaborative OpenLearning website on ALD is under construction [7]. Many of the images used in this tutorial—and in Refs. 6 and 7—are available in Wikimedia Commons [8] for easy and free reuse. To contribute to collective learning of the early history of ALD, the open-science effort Virtual Project on the History of ALD [4] still welcomes new volunteer participants.

[1] E. Ahvenniemi et al., J. Vac. Sci. Technol. A 35 (2017) 010801 (2017).

[2] R.L. Puurunen, ECS Transactions 86 (6) (2018) 3-17; OA: DOI:10.1149/osf.io/exyv3

[3] G.N. Parsons et al., J. Vac. Sci. Technol. A 38 (2020) 037001.

[4] http://vph-ald.com

[5] J.R. van Ommen, R.L. Puurunen, ALD 2020, https://youtu.be/jqm_wf49WwM

[6] J.R. van Ommen, A. Goulas, R.L. Puurunen, Kirk-Othmer Encyclopedia on Chemical Technology, submitted.

[7] http://openlearning.aalto.fi, ALD

[8] https://commons.wikimedia.org/wiki/Category:Atomic_layer_deposition

11:45am **TS1-SuM-22 Let's Talk Dirty - Battling Impurities in ALD Films*, Henrik Pedersen,*** Linköping University, Sweden **INVITED**

The success of ALD stems from the self-limiting nature of ALD, allowing ALD to deposit film with perfect conformality, very high uniformity, and excellent thickness control. The self-limiting nature of ALD, in turn, stems from the formation of monolayers stable enough to survive until the next pulse of reactive species. The survival of the monolayer sets an upper temperature limit for ALD and thereby an interesting challenge for the design of precursor molecules. But it also sets a challenge for managing film impurities: unwanted atoms in the ligands of the precursors are less likely to desorb from the surface at lower temperatures, creating unwanted impurities in ALD films.

In the ALD community we are quick to highlight all the nice features of ALD, but we are, perhaps naturally, less keen to discuss all the problems associated with ALD films. Film impurities is one of these problems which we do not always talk about. It is not because we do not understand the impurities or can measure them, but perhaps, partly, because we do not fully see the severity of the problem. Impurities in ALD films affect device performance by increasing leakage currents, capacitance, and electrical resistivity, and thereby decrease endurance, reliability, and cyclability of the final device. Film impurities can also badly affect the crystallinity of the film and obstruct epitaxial film growth.

Impurities in ALD films can emanate from the precursors, the carrier gas, the ALD reactor, the substrate and post-deposition handling. In this tutorial I will discuss what can be done to battle impurities from these sources. I will also compare ALD grown films with films deposited by other techniques to try to show how well ALD is doing against its competition.

12:35pm **TS1-SuM-32 Seeing Is Believing: *In situ* Techniques for Atomic Layer Deposition (ALD) Process Development and Diagnostics*, Parag Banerjee,*** University of Central Florida **INVITED**

Atomic layer deposition (ALD) has reached manufacturing scalability in industries such as, semiconductors, energy and catalysis. It is estimated that by 2025, ALD will have a market cap of ~$3.05 billion while making inroads into new industries such as, pharmaceuticals, paint products, and optics. The success of ALD as a process platform is heartening to observe, though old challenges and new bottlenecks in ALD continue to create scientific and engineering opportunities in developing new chemistries and innovation at the hardware level. One such aspect of ALD is the concurrent development and growth of *in situ* techniques that has, 1) led to a deeper understanding of the complex surface chemistries at play during an ALD process and, 2) provided a real-time platform for flagging process deviations and excursions of established ALD processes.

The use of *in situ* techniques in ALD is as old as ALD itself. In this tutorial session, I will provide a comprehensive review of *in situ* techniques published in ALD literature. These can be classified into two categories. One, where new process chemistries are unraveled. These techniques include Fourier transform infrared spectroscopy (FTIR) and quadrupole mass spectrometry (QMS). A second class of techniques involve observing physical changes to the film, such as gravimetric changes or film thickness. These techniques include quartz crystal microbalance (QCM) and spectroscopic ellipsometry (SE). Both these classes of techniques can be applied to 1) rapidly develop and optimize new ALD processes or 2) monitor established ALD processes and detect changes to deposition characteristics over time. Every technique has its set of advantages and drawbacks and practitioners of ALD will do well to understand these constraints. How well an *in situ* technique works in a scenario depends on multiple factors including hardware flexibility, process complexity and required throughout. The tutorial session will end with some emerging *in situ* techniques that are creatively applied to understand ALD processes. The potential for machine learning and advanced data science techniques to sift through massive amounts of *in situ* data will be touched upon.

1:25pm **TS1-SuM-42 ALD Powder Manufacturing***, **Arrelaine Dameron,*** Forge Nano **INVITED**

Atomic Layer Deposition (ALD) has been demonstrated to impart significant processing and performance gains in all areas of advanced materials in addition to semiconductor and other wafer applications. ALD is a well utilized platform technology for powders, porous particles, and high-surface area objects that has been widely demonstrated throughout the literature. Fundamentally, ALD on powders or any high surface area surface is the same as on flat surfaces. Simplistically, as long as the chemistry is self-limiting, the precursors can be kept separate and supplied at a concentration to saturate the available surface area, the thin film growth will be controlled and uniform. In practice, the very high surface area, long diffusion pathways, and complexities of gas solids mixing bring a few additional challenges not usually encountered during lab-scale ALD.

Historically ALD has been regarded as a lab-only process outside of semiconductor manufacturing, disregarded as too expensive and an unrealistic process for commercial adoption. However, several methods for high-throughput and scaled-batch manufacturing have been developed over the last decade, making ALD on powders affordable as a material-upgrading technique. Forge Nano has patented, constructed, and demonstrated the highest throughput ALD capability in the world, unlocking new potential for lower cost integration of ALD into products.

This tutorial will cover the basic equipment and process procedures for powder ALD at the lab scale, and equipment and particle ALD manufacturing methodologies. Additionally, it will provide some real-world examples of high surface area ALD applications in a spectrum of technologies ranging from pigments to catalysis and the most appropriate steps towards the industrialization of ALD-enabled materials for some of the application examples. The intent of this seminar is to identify the critical processing and scaling challenges for high surface area and powdered materials to enable more research opportunities and a greater breadth of commercial technology.

2:10pm **TS1-SuM-51 Closing Remarks & Thank You!***, **Scott Clendenning,*** Intel

Thank you for attending today's Tutorial Session! We will see you tomorrow at the Virtual Meeting!

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