

Tuesday Afternoon, June 30, 2020

Tutorials

Room Live - Session TU1-TuA

Tutorial Session: Tuesday Live

Moderators: Christophe Detavernier, Ghent University, Belgium, Harm C.M. Knoops, Oxford Instruments Plasma Technology, The Netherlands

1:00pm **TU1-TuA-1 Tuesday Tutorial Welcome & Sponsor Thank You, *Christophe Detavernier***, Ghent University, Belgium

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1:15pm **TU1-TuA-2 ALD Precursor Chemistry: Synthetic Routes, Purification and Evaluation of Precursors, *Anjana Devi***, Ruhr University Bochum, Germany **INVITED**

An open challenge for forefront research is provided by innovative strategies based on the synergic combinations of precursor chemistry and material synthesis, opening new horizons for the development of advanced functional material systems. In the case of atomic layer deposition (ALD), the important figure of merit is the precursor. High volatility, reactivity and thermal stability are the main requirements for an ALD process. But several precursors do not possess all of these characteristics. Thus, the search for alternative precursors continues to grow to overcome the drawbacks associated with the well-established or commercially available precursors in order to meet the stringent demands for modern technological applications. The reports on the design of new precursors by systematic and logical variation of the ligand sphere remains a rare occurrence in literature. Apart from identifying new and suitable precursors for ALD, it is also important that the precursors can be synthesized and scaled up to larger batches, they are non-toxic and the purity of the product is of high relevance. In this presentation, the approaches taken to synthesize different classes of precursors, their purification and the methods employed to characterize them will be discussed. The focus will be on representative precursors for metals and metal oxides and evaluating the precursor purity, volatility, thermal stability relevant for ALD applications.

2:15pm **TU1-TuA-6 Atomic Layer Engineering: Hardware Considerations for ALD System Design and Process Development, *Neil Dasgupta***, University of Michigan **INVITED**

As the portfolio of ALD processes chemistries continues to broaden, there is an increasing need for hardware customization to ensure process compatibility. Furthermore, the manufacturing demands for ALD continue to push for higher throughput, without sacrificing film quality or process reliability. In particular, as the form factor of ALD substrates begins to deviate from planar wafers to 3-D architectures, coupled thermal, mass transport, and chemical kinetics play an increasingly important role in ensuring optimal ALD deposition. This tutorial will describe several critical, and often under-discussed, aspects of ALD reactor hardware design and process control. The discussion will begin with a primer on vacuum system design in general – materials compatibility, fittings, o-rings/gaskets, valves, flow controllers, pumps, and metrology tools. Next, precursor delivery to the substrate will be discussed, with consideration of special challenges for solid precursors and low-vapor pressure precursor delivery. Various chamber geometries will be compared, and the coupled thermal/fluid transport behavior during vapor transport and reactivity will be described. Incorporation of in situ process metrology will be described. Finally, vacuum exhaust line design will be discussed, with an emphasis on maintaining a safe, and reproducible system.

3:15pm **TU1-TuA-10 ALD on High Aspect Ratio and Nanostructured Materials: from Fundamentals to Economics, *Angel Yanguas-Gil***, Argonne National Laboratory **INVITED**

The ability to conformally coat high aspect ratio and nanostructured substrates over large substrate areas is one of atomic layer deposition's enabling capabilities. From the coating of trenches and vias to the extreme case of polymer infiltration, there are numerous examples in the literature illustrating how ALD's self-limited behavior can enable new architectures and applications. In this tutorial I will focus on the fundamental aspects of the coating of high surface area materials, and in particular how the surface chemistry affects the dynamics of infiltration, scale up, and tradeoff between throughput and precursor utilization. After a brief introduction summarizing experimental approaches for both growth and characterization techniques and some conventional and extreme applications, I will explore the impact that shape, pore size, the overall

microstructure of nanostructured substrates, and precursor-surface interaction have on an ideal ALD process. The impact of these parameters can be codified in a few compact expressions that help us visualize and explore the scalability of a given ALD process. I will then move on to consider how other aspects of the surface chemistry, such the presence of surface recombination or deactivation pathways, ligand-surface interactions, and non self-limited and soft-saturating components affect conformality. I will also look at the coating of nanostructured materials from a reactor scale perspective, exploring through simple models and experimental observations how precursor transport is disrupted by the presence of high surface area substrates in both cross flow and static dose configurations, two of the most common experimental approaches. I will then conclude with an overview of experimental challenges and gaps in our understanding that, if solved, could help accelerate the development of novel processes involving high aspect ratio and nanostructured substrates.

4:00pm **TU1-TuA-13 Questions & Answers, *A Devi***, Ruhr University Bochum, Germany; *N Dasgupta*, University of Michigan; *A Yanguas-Gil*, Argonne National Laboratory

Feel free to ask questions to our panel of Tutorial presenters

4:30pm **TU1-TuA-15 Session Over - View On Demand Presentations, *C Detavernier***, Ghent University, Belgium; *Harm C.M. Knoops*, Oxford Instruments Plasma Technology, The Netherlands, Netherlands

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Wednesday Afternoon, July 1, 2020

Tutorials

Room Live - Session TU2-WeA

Tutorial Session: Wednesday Live

Moderators: Paul Poodt, Holst Centre / TNO, Erwin Kessels, Eindhoven University of Technology, the Netherlands, Jean-François de Marneffe, IMEC

1:00pm **TU2-WeA-1 Wednesday Tutorial Welcome & Sponsor Thank You, Paul Poodt**, TNO/Holst Center, The Netherlands, Netherlands

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1:15pm **TU2-WeA-2 Growth Mechanisms and Selectivity During Atomic Layer Deposition, Annelies Delabie**, KU Leuven – University of Leuven/IMEC, Belgium

INVITED

Area-selective deposition (ASD) holds the potential to build nanostructures from the bottom up, only where needed, with atomic precision in both vertical and lateral direction. The technique is of great interest for nano-electronic device manufacturing, as it can be applied for bottom-up deposition in small trenches or holes, or to create nanoscale structures with great accuracy by self-alignment. In addition, ASD can simplify complex integration flows and is a cost-effective approach that consumes less chemical products and energy as compared to traditional top-down patterning. Today, many materials can be deposited by atomic layer deposition (ALD), but only few ALD processes show selectivity. ASD is governed by a complex interplay of several processes, including adsorption, desorption, surface reactions and diffusion. Fundamental understanding of the mechanisms during ALD can contribute to the design of new ASD processes for a wider range of materials. This tutorial will therefore first address the growth mechanisms during ALD on an initially homogeneous substrate surface. Several quantitative growth models have been proposed to describe the initial ALD growth regime. Next, we discuss the mechanism of ASD in nanoscale patterns, and how the growth behavior during ASD can differ from regular growth on homogeneous substrates. Finally, we address strategies to minimize deposition in the non-growth surface area, while simultaneously maintaining or enhancing growth on the growth surface area.

2:15pm **TU2-WeA-6 Self-limiting Surface Reactions for Atomic-level Control of Materials Processing, Simon D. Elliott**, Schrödinger, Inc. **INVITED**

ALE and ALD have in common that their defining characteristic is a self-limiting transformation of the surface in each cycle. This leads to the well-known advantages of the techniques - uniformity, conformality and digital control of thickness etched/deposited. In this tutorial we will examine how the chemical interaction between a gas and a surface can be either self-limiting or continuous. Looking at how this depends on process conditions (temperature or pressure) gives a straightforward way to understand the process window and account for the etch/growth rate. The simple procedure for estimating etch/growth rates from surface coverage will be presented. We will discuss the various potential sources of self-limiting chemistry, such as the concentration of substrate sites, availability of co-reagent fragments, exposure of gaseous reagent and diffusion along the surface. Examples will be given from both acid-base and redox-based chemical mechanisms of ALE and ALD.

3:15pm **TU2-WeA-10 Fundamentals of ALE – Optimizing Passivation and Etch*, Mark Kushner**, University of Michigan **INVITED**

The ideal process of plasma based atomic layer etching (ALE) consists, in principle, of two independent self-limiting steps. The first is passivation of an atomically smooth surface with plasma produced radicals with the goal of lowering the binding energy of the surface resident atoms. The second is removal of the passivated layer of atoms with the activation energy provided by plasma generated ions of carefully controlled energies. Ideal ALE, the removal of a single monolayer per cycle, is rarely achieved. There are narrow process windows in terms of how much activation energy can be delivered during the passivation step and how many passivants can be present during the etch step. In addition to the intrinsic chemistry of the ALE process, the quality of the process is ultimately determined by how well the fluxes delivered by the plasma to the surface can be controlled – all of which contribute to the ideality of the process. ALE of dielectrics (ALE-D), typically using fluorocarbon gas mixtures, proceeds through deposition of a thin polymer layer which provides the precursors for the etch step. As such, ALE-D begins as being non-ideal as the passivation step is not self-

limiting. ALE-D is perhaps better described as controlled EPC (etch-per-cycle). Depending on polymer thickness and ion energies, the EPC can be a fraction of monolayer or many monolayers. In this tutorial, ideal and non-ideal ALE processes will be reviewed with an emphasis on the plasma properties required to achieve ideal behavior. Examples will be used from computer modeling of reactor scale plasma generation of passivants and etchants, and feature scale profile simulation. Halogen plasma based ALE of conductors will be used to illustrate the process window requirements for ideal EPC. Simulation of ALE-D of SiO₂ and Si₃N₄ will be used to illustrate how control of plasma properties can produce controlled EPC, selectivity and surface smoothness. * Work supported by Lam Research Inc., TEL Technology Center America LLC and Samsung Electronics.

4:00pm **TU2-WeA-13 Questions & Answers, M Kushner**, University of Michigan; **A Delabie**, KU Leuven – University of Leuven/IMEC, Belgium; **S Elliott**, Schrödinger, Inc.; **Jean-François de Marneffe**, IMEC, Belgium
Feel free to ask questions to our Tutorial presenters

4:30pm **TU2-WeA-15 Session Over - View On Demand Presentations, Erwin Kessels**, Eindhoven University of Technology, Netherlands
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