Thin Films
Room 115 - Session TF+AP-MoA

Thin Films Special Session: Remembering Dr. Paul Holloway II & Reception

Moderators: Sean Jones, Argonne National Laboratory, **Philip Rack**, University of Tennessee

1:30pm **TF+AP-MoA-1 A Surface Science Approach to Advancing Area-Selective Deposition and Atomic Layer Etching**, ***Adrie Mackus,*** Eindhoven University of Technology, Netherlands **INVITED**

With future nanoelectronics relying on the vertical stacking of devices, selective deposition and etching techniques are essential for enabling self-aligned processing of materials on such 3-dimensional devices structures. Similar to the research approach of dr. Paul. H. Holloway, in this work surface science methods are employed to obtain understanding of thin film processing. A combination of in-situ experiments and simulations is carried out to study the mechanisms of selectivity and inhibition.

Our work on area-selective atomic layer deposition (ALD) involves the use of small molecule inhibitors (SMIs) in three-step ALD cycles.[1] For example, diketone molecules can be used to inhibit the growth on various oxides surfaces. In-situ infrared spectroscopy studies previously revealed that the diketone acetylacetone (Hacac) can adsorb on an Al_2O_3 surface in chelate and monodentate adsorption configurations.[2] Inspired on these insights, we recently developed atomic layer etching (ALE) processes based on etching by diketone dosing (e.g., hexafluoroacetylacetone) and plasma cleaning steps. Infrared spectroscopy and simulation studies suggest that the mechanism of etching with diketones involves a competition between etching and inhibition reactions. In this presentation, I will discuss how inhibition reactions can be exploited for achieving either area-selective ALD or ALE, and highlight how surface science methods are crucial for understanding the underlying mechanisms.

1. Mackus *et al., Chem. Mater.* **31**, 2 (2019)
2. Merkx *et al., Chem. Mater.***32**, 3335 (2020)

2:00pm **TF+AP-MoA-3 Tuning Surface Radical Species for Area-Selective Initiated Chemical Vapor Deposition of Polymer Thin Films**, ***Junjie Zhao,*** Zhejiang University, China **INVITED**

Self-aligned bottom-up growth of polymer thin films is desired for non-lithographic patterning in applications ranging from nanostructure fabrication to device integration. Aiming at achieving area-selectivity for initiated chemical vapor deposition (iCVD), we developed a toolkit to tune the local concentration of radicals and thus the surface polymerization kinetics. We found that the radical concentration can be promoted locally by (1) generation on targeted surfaces, (2) trapping through gradient forces, and (3) retainment *via* reversible dormant species. *In-situ* quartz crystal microbalance was employed to investigate the reaction mechanisms involved in these area-selective iCVD processes. Cross-sectional imaging and spectroscopic microscopy confirmed the high selective of polymer deposition on the growth areas. Finally, we will show that these strategies are generally effective for area-selective deposition of poly(glycidyl methacrylate), poly(divinylbenzene) and cyclosiloxane polymers.

2:30pm **TF+AP-MoA-5 Recent Trends in Thermal ALD Chemistry**, ***Markku Leskelä,*** *G. Popov, M. Mattinen, A. Vihervaara, M. Ritala,* University of Helsinki, Finland

A review published in 2013 listed all the two-precursor ALD processes reported by the end of 2010 [1]. Since then, many new materials have been deposited by ALD and new processes have been developed for earlier known ALD materials. The recently published ALD database aims to provide a crowdsourced up-to-date collection of ALD processes [2]. In this presentation, we highlight the new precursor and thermal process chemistries published after 2010 based on the ALD database.

The data base contains 1725 unique thermal ALD processes for 548 thin film materials published between 1975 and 2023. The boom in ALD started around 1995 and the number of new processes reported annually increased from 20 in early 1990s to 60 in 2008. Since then, the number of new processes has remained at 60-80 each year. Since 2010, 991 new processes have been published for 441 materials from which 316 materials did not earlier have any ALD process.

Oxide processes form more than 50 % of all the published processes but their share has slightly decreased after 2010. Processes for chalcogenides, pnictides and elements are next in the list. Binary compounds clearly dominate the materials but after 2010 ternary and quaternary compounds as well as elements have increased their share. The number of new ternary processes is roughly double compared to new binary processes. From the ternary and quaternary compounds about 75 % are oxides. Before 2010 the five most common ligands used in metal precursors were halides, alkoxides, alkyls, β-diketonates and amides/imides. The order changes after 2010 to amides/imides, cyclopentadienyls, halides, alkoxides, and alkyls. Heteroleptic complexes have increased their share during the last decade. In non-metal precursors, reducing agents increased importance because of the increased interest to metal deposition.

New elements added to the ALD portfolio since 2010 are alkali metals (Na, K, Rb, Cs), Be, Re, Os, Au and Sb, the first five as oxides and latter four as elements. Reductive processes for transition metals are sought and first thermal processes have been reported for tin and chromium.

86 new binary materials were deposited by ALD since 2010 the biggest group being chalcogenides (29), halides (15) and oxides (15). These materials are linked to broader material and application trends, including perovskite solar (halides) and 2D materials (chalcogenides). Disulfide processes have been reported for Zr, Hf, Mo, Nb, Sn, Re and diselenides for Mo and W.

References

[1] V. Miikkulainen, M. Leskelä, M. Ritala, R.L. Puurunen, J. Appl. Phys. 113, (2013) 021301.
[2] https://www.atomiclimits.com/alddatabase/

2:45pm **TF+AP-MoA-6 Ultrathin Polymers Films: Smart Materials and Functionality**, ***Rigoberto Advincula,*** University of Tennessee Knoxville

Nanostructuring involves the application of materials and processing methods to achieve unique dimensional structures at the nanoscale. Soft matter looks at polymers and the self-assembly and directed assembly of macromolecules that results in a unique function, e.g. sensors, electronic actuators, microfluidics, etc.. The research and development of smart or intelligent surfaces and coatings capable of stimuli-response or Omni behavior represent an essential development for coatings in any major application. The ability to control wetting through nanostructuring and choice of chemical functionality can be supplemented by the right deposition methods or application of both lithographic and non-lithographic printing methods. In particular, we have used: 1) polymer grafting, 2) polyelectrolyte layer-by-layer deposition, 3) molecular imprinting of polymers, 4) electro-nanopatterning method using conducting AFM and 5) colloidally templated arrays. Until now, colloidal template 2D electropolymerization remains largely an unexplored method, and there are only a few accounts on colloidal template electropolymerization techniques for micropatterning polymer films. But combined with electropolymerization and polymer brushes it is possible to have functional polymer films that can have sensing and controlled wettability. We will be reporting on the use of stereolithographic lithography (SLA) to create functional superhydrophobic surfaces and nanoreactors.

3:00pm **TF+AP-MoA-7 Growing Polymers Molecule by Molecule Through Vapor Deposition**, ***Matthias J. Young,*** University of Missouri-Columbia; *N. Paranamana, M. Mehregan, S. Mehregan, A. Datta,* University of Missouri, Columbia **INVITED**

Controlling the sequence of monomers within a copolymer is challenging. Solid-phase peptide synthesis provides molecular sequence control of amino acids by employing solution-phase synthesis with removable protecting groups. This technique was awarded a Nobel prize in 1984 and has spawned a revolution in molecular biology and biochemistry over the last fifty years. However, this approach for peptide synthesis is not readily transferrable to other classes of polymers. Here, we summarize our efforts over the last five years to provide molecular sequence control in polymers formed by oxidative polymerization by employing self-limiting vapor-phase surface reactions through a process termed oxidative molecular layer deposition, or oMLD. We describe insights into the mechanism of oMLD growth that facilitates molecular sequence control, and we examine how molecular sequence impacts redox activity and electronic conductivity. We discuss the various oMLD homopolymer and copolymer chemistries that have been developed to date, expanding from the first oMLD homopolymer chemistry in 2014 to seven oMLD homopolymer chemistries in 2024, and the outlook for oMLD growth of hundreds of potential homopolymer chemistries and a factorial number of copolymer chemistries. We demonstrate the ability to form ultrathin conformal polymer coatings by oMLD and we discuss the application of these thin film coatings to electrochemical energy storage and ion sensors. We also discuss

opportunities for improving on current oMLD synthesis techniques and how the knowledge we have gained about oMLD growth may inform the development of other layer-by-layer vapor-phase polymerization chemistries.

3:30pm **TF+AP-MoA-9 Solar Cells, Sensors, and Sensorimotor Neural Prosthetics: My Branch of the Holloway Tree***, **Loren Rieth**,* West Virginia University **INVITED**

Professor Paul Holloway was my PhD mentor from 1994 to 2001. “Doc's” combination of down-to-earth practicality, erudite knowledge of fundamental materials science, absence of hubris, and mischievous sense of humor resonated with me then and now. His passion for science and engineering was clear from the hours he kept (his modest car was always one of the first to arrive in the morning), his joy when learning something new, and the sustained research productivity he achieved. He balanced this with helping Bette run the family farm, hunting gators, and a love for the Florida outdoors. It was an honor, privilege, and joy to have him as a mentor. The exemplary training I received in the Holloway group on thin film semiconducting materials for solar cell included vicarious learning about luminescent and optical materials and Ohmic semiconductor contacts. This led to my research in metal oxide gas sensors, harsh environment MEMS, and ultimately neural interface microelectrode research and development, the focus of my technical talk.

My neural interface research focuses on penetrating neural electrodes based on micromachined silicon, and flexible neural interfaces based on polyimide microfabrication. Rapid progress is being made in technologies to record, stimulate, and modulate the nervous system. These advancements are being made both to treat diseases with new medical device technologies, and also as tools for basic neuroscience research. Treatments enabled by neural interfaces include controlling bionic limbs for patients with amputations or paralysis, restoring senses (hearing, vision, and touch), treating inflammatory diseases, controlling metabolic diseases, helping to restore mental health, and many others. Currently, successful devices such as cochlear implants, deep brain stimulators, and vagus nerve stimulators, rely on macro-electrodes fabricated using bulk materials. This limits their ability to scale towards interfacing the billions of neurons that comprise the nervous system. Materials science plays a critical role in the development penetrating and flexible micro-electrode technologies. I’ll highlight development and use of Utah Slanted Electrode Arrays in the peripheral and central nervous system, and their associated materials challenges. Additionally, recent developments regarding advanced polyimide-based flexible electrodes and optical neural interfaces for small (e.g. 100 µm diameter) peripheral nerves will be presented. An important example is the vagus nerve of murine models, which can be modulated to regulate the autonomic nervous system, a technique called bioelectronic medicine.

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