From Ionic Crystals to Ionic Conductivity: An Iconic Celebration of Gary W. Rubloff's 50+ Years in Science
Room 317 - Session GWR-MoM

From Ionic Crystals to Ionic Conductivity: A Special Celebration of Gary W. Rubloffs 50+ Years in Science

Moderators: Parag Banerjee, University of Central Florida, **Keith Gregorczyk**, University of Maryland, College Park, **Alexander Kozen**, University of Vermont

10:00am **GWR-MoM-1 Recent Advances in Electrochemical Memory*, Alec Talin,*** Sandia National Lab **INVITED**

Over the past several decades, electronics have relied on deterministic, binary states accessed by electrons to store and process information. The challenge of physical scaling of this approach motivates the need for post-CMOS or post-digital analog approaches to increase functional density and energy efficiency. Instead of using only electron motion to encode information, analog electronics can use electrical, thermal and electrochemical gradients in various heterogeneously integrated materials to move electrons, ions, and domains. Understanding the scientific basis of these complex, frequently coupled mechanisms is difficult, resulting in few reliable physics-based models that can be used by circuit and chip designers. These mechanisms also present increased sensitivity to variability, noise, and poorly controlled kinetic processes. As such, despite decades of research and promising laboratory-scale performance, knowledge gaps in the features of analog electronics have led to their consistent failures to meet the stringent requirements needed for their commercialization. In my presentation, I will discuss our recent work to address these challenges using 3-terminal electrochemical random access memory (ECRAM)[1] that encodes information in three dimensional volumes, rather than 2-dimensions channels or 1-dimensional filaments and combines thermodynamic and kinetic mechanisms to stabilize a high density of analog states.

(1) Talin, A. A.; Meyer, J.; Li, J.; Huang, M.; Schwacke, M.; Chung, H. W.; Xu, L.; Fuller, E. J.; Li, Y.; Yildiz, B. Electrochemical Random-Access Memory: Progress, Perspectives, and Opportunities. *Chem. Rev.* **2025**, *125* (4), 1962-2008. DOI: 10.1021/acs.chemrev.4c00512.

10:15am **GWR-MoM-2 Advancing New Semiconductor Materials and Devices Thought Characterization and Metrology*, Alain Diebold,*** CNSE, University at Albany **INVITED**

In 1994, Gary Rubloff and Michael Liehr started the AVS Manufacturing Science and Technology Group.The first MSTG sessions were all invited talks that provided a thorough look at silicon integrated circuit manufacturing technology and the associated R&D.Characterization and metrology activities enabled materials and process R&D and increased the yield during manufacturing.In the 1990's transistor devices were planar and on-chip interconnect transitioned from planar aluminum wiring.The next step was Damascene copper interconnect.The new metallization technology brought higher aspect ratio structures which required improved processing and metrology.Then 3D FinFET transistors with hafnium based dielectric layers were introduced again pushing characterization and metrology.Today, the most advanced transistors have vertically stacked channels with gate-all-around dielectric metal technology. Memory technology has very high aspect ratio structures with more than 100 layer stacks.This talk will outline some of the advances in characterization and metrology that have critical enablers for today's technology.The methods that will be covered include spectroscopic ellipsometry, high resolution X-Ray diffraction, scanning electron microscopy for critical dimensions, scanning transmission electron microscopy, and associated advances.

10:30am **GWR-MoM-3 Materials, Technologies, and Systems Integration: How Gary Rubloff Inspired Me to Be a Better Microsystem Researcher*, Reza Ghodssi,*** University of Maryland College Park **INVITED**

It is a distinct honor to participate in this symposium celebrating Prof. Gary Rubloff's extraordinary contributions to science and engineering. As a colleague at the University of Maryland for more than two decades, I have had the privilege of witnessing first-hand Gary's leadership in fostering interdisciplinary research at the intersection of materials science, electrochemistry, energy systems, and microscale technologies. His vision for collaborative, translational research has inspired a vibrant innovation ecosystem and helped shape many of the interdisciplinary directions pursued by my research group.

In this talk, I will highlight the evolution of integrated micro- and nanosystems developed by my group over more than three decades. I will discuss how we have leveraged foundational MEMS technologies, advanced microfabrication techniques, and systems integration methodologies to develop platforms for sensing, actuation, microfluidic bioMEMS, microscale energy storage and harvesting, including three-dimensional battery architectures, microfabricated electrochemical systems, and self-sustaining power solutions for embedded devices.

I will then describe the translation of these technologies into biomedical and clinical applications, including ingestible capsule devices for gastrointestinal sensing, tissue sampling, drug delivery, and physiological monitoring. The focus of this work is to enable in situ diagnostics and therapeutic interventions, toward gastrointestinal health, biofilm monitoring and inhibition, and platform technologies for investigating gut-brain interactions. Together, these research activities demonstrate how advances in systems integration can be translated into impactful solutions for energy, healthcare, and society, reflecting the interdisciplinary spirit and strong mentoring that have characterized Gary Rubloff's distinguished career.

10:45am **GWR-MoM-4 Biofabrication in Microfluidics for Biological and Fuel Cell Challenges: Inspired by Gary's Innovation Path*, Xiaolong Luo,*** Catholic University of America **INVITED**

In this talk, I will discuss biofabrication in microfluidics, a significant side path in Gary's extraordinary semiconductor career that enables us to tackle some formidable challenges in biology and fuel cells. First, I will introduce biofabrication in microfluidics and the tools developed to integrate biology with microdevices, including electrodeposition, flow assembly at flow interfaces, and electrofabrication with distal electrodes. Second, the presentation will cover some biofabrication-enabled microfluidic platforms addressing biological and biomedical challenges, ranging from lipid bilayer to tissue-on-a-chip, from model biofilms to microbiome-on-a-chip and biofilm sensors, and from bacterial chemotaxis to rapid antibiotic susceptibility testing for timely sepsis treatments. Finally, I will introduce distal electrofabrication of chitosan membranes on printer paper as anion-exchange membranes for direct methanol fuel cells, with the potential to dramatically lower fuel cell costs for broader civil adaptation.

11:00am **GWR-MoM-5 Hidden Chemistry and Unexpected Pathways in Atomic Layer Deposition*, Theodosia Gougousi,*** UMBC **INVITED**

Atomic Layer Deposition (ALD) is often described as an ideal, self-limiting thin-film growth process governed by simple ligand-exchange reactions. While this simplified reaction scheme is successful, in general, there is growing experimental evidence that real ALD chemistries are far more complex, involving competing and parallel reaction pathways,resulting in unexpected thin-film properties.

In this talk, I will present a series of examples showing how subtle variations in precursor chemistry, process temperature, and substrate surface condition can activate parallel and competing reaction pathways that strongly influence interfacial quality and structure, as well as film composition and properties. For example, in simple ALD metal oxide chemistries, I will discuss unexpected phenomena such as precursor decomposition during nominal ALD cycles, transport of interfacial species through growing films, and non-monotonic changes in optical and electrical properties within commonly assumed "ALD windows." In situ and ex situ spectroscopic measurements reveal that these effects arise from hidden chemical processes that persist well beyond initial surface coverage and are highly sensitive to both precursor identity and processing conditions.

These results highlight the limitations of overly simplified growth models and underscore the need to consider the complete ALD chemistry when selecting processes and materials for specific applications. Understanding these hidden pathways is essential for improving process control and reproducibility and for exploiting ALD as a platform for discovering new material behavior.

11:15am **GWR-MoM-6 From Stress Gradients to Reaction Fronts: Physics-Based Modeling for Next-Generation Ionic Devices*, David Stewart, Yueming Song,*** University of Maryland, College Park*; Binh Hoang, Chuan-Fu Lin,* Catholic University of America*; Paul Albertus, Gary Rubloff,* University of Maryland, College Park **INVITED**

Electrochemical modeling is essential to the development of advanced energy storage devices. In research and industry, finite element models with standard governing equations are commonly used to predict battery performance with different structural parameters such as particle grain size or porosity. However, electrochemical modeling is far from a static field that

can simply be a plug-and-play solution to designing electrochemical devices. In this presentation we will discuss key results from a decade of work in electrochemical modeling, including 3D architecture design, self-regulating behavior, and the opportunities for measuring and leveraging dynamic material properties exhibit by ionic materials.

In the Rubloff group, we have used these governing equations to predict performance metrics for 3D batteries based on thin film manufacturing techniques. 3D structures have been modeled at the level of pure electrochemistry and including various forms of electro-chemo-mechanical coupling and a stark contrast emerged in the forces that governed Li flux. Most importantly, while GPa levels of stress gradients are predicted to form in a cell using brittle TiO_2 and V_2O_5 electrodes, electro-chemo-mechanical coupling can serve as a self-regulating force, diverting Li flux away from the high stress areas and preventing severe stress-delamination.

While these simulations offer important guidance on cell design and experimental measurements, key to an accurate prediction are dynamic material properties such as the ionic diffusivity, partial molar volume, and electrical conductivity which vary with lithiation state. An important example are FeF_3 electrodes, which exhibit a variable electronic conductivity across several orders of magnitude. The consequence is that the distribution of the lithiated, high conductivity phase, governs the propagation of the electrochemical reaction. We use a patterned current collector to create a 5 mm lateral distribution of Li in thin film FeF_3 electrodes, and show excellent agreement with experimental results. Current concentrates at the reaction front, preventing full lithiation until conductivity equalizes across the electrode, which spreads linearly with time.

We expect these phenomena to play important roles in future ionic device designs such as electrochemical RAM (which leverages dynamic conductivity for in-memory computing). As devices scale, there will be an ongoing competition between self-regulating forces and geometric inhomogeneities which ultimately governs device response. Capturing this competition accurately will require physical and chemical models continuously validated against experiment.

11:30am **GWR-MoM-7 Operando Electrochemical Phase Engineering Platform for Nanocomposite Thin Films***, **Daniela R. Fontecha**, Osma J. Gomez, Nam Kim, Sang Bok Lee, Gary W. Rubloff, Keith E. Gregorczyk,* University of Maryland College Park **INVITED**

Nanoscale materials processing advancements have enabled on-chip ionic devices like microbatteries, super capacitors, ion-gated transistors, etc. using standard semiconductor processes (such as atomic layer deposition - ALD) to develop electrochemically active thin films. However, challenges remain in understanding and controlling ionic and electronic transport in nanoscale systems. Nanoscale ionic systems that are tunable at multiple scales (chemical composition, phase distribution, and crystal structure) are critical in understanding how these parameters affect transport and materials properties. In this work we demonstrate a system with these qualities and introduce an additional lever - *operando* electrochemical phase engineering - to systematically control the phase distribution that allows us to study the effects of individual phases on ionic transport in a ternary-phase ALD nanocomposite.

We study a Li-Ti-P-O semicrystalline nanocomposite, which consists of nanocrystalline lithium titanium phosphate (LTP) and anatase TiO_2, both embedded in an amorphous Li-Ti-P-O matrix. This nanocomposite thin film system can be synthesized by alternating between titanium phosphate and lithium oxide ALD sub-processes (resulting film depicted in **Figure 1a**), where changing the ratio of oxide-to-phosphate thickness enables compositional tunability while post-process annealing allows for control of crystalline phases in the system. We demonstrate, through electrochemical phase engineering, a voltage-dependent materials system that converts between high power and high capacity by removing the crystalline LTP phase operando. In the high power voltage window (2.1 V – 3.5 V vs Li^+/Li), depicted in **Figure 1b**, the nanocomposite retains 60 % of its initial capacity (125 mAh/g) at an ultrafast charging rate of 200 C (18 sec). In the high capacity voltage window (0.25 V – 3.5 V vs Li^+/Li), the nanocomposite without crystalline LTP (**Figure 1c**) delivers 1302 mAh/g at 1 C and retains 61.9 % of its initial capacity at a charging rate of 20 C (3 min).

In this talk I will discuss how we combined composition-controlled ALD films with voltage-window-selective cycling to drive controlled evolution of crystal structure, phase distribution, and internal interfaces. Most importantly, we use this control to isolate the contribution of each constituent phase to the overall electrochemical behavior of the system. This work establishes the Li-Ti-P-O nanocomposite as a tunable platform for studying how crystal structure and interfaces govern transport in thin ionic films — with direct relevance to thin film microbatteries & ionic supercapacitors.

11:45am **GWR-MoM-8 Pyridine-Catalyzed Molecular Layer Deposition of Silicon Oxycarbide***, **Gregory Parsons**,* Department of Chemical & Biomolecular Engineering*; Man Hou Vong, Seoyeon Kim, Michael Dickey,* North Carolina State University

Hydrogenated silicon oxycarbide (SiOC-H) is a common low-permittivity dielectric material in integrated circuits. As integrated circuits continue to downsize, SiOC-H deposition processes, such as molecular layer deposition (MLD) that offer precise thickness control and high conformity are increasingly vital. MLD of SiOC-H using bis(trichlorosilyl)methane and water satisfies these demands via self-limiting surface reactions. Herein, we introduce the use of pyridine in the precursor dosing step to catalyze SiOC-H MLD, resulting in a growth per cycle (GPC) of 0.31 nm/cycle, 2x larger than previously reported, and ten times larger than observed under identical conditions without catalyst present. Upon annealing at 250 – 550 °C, the Si–CH_2–Si and Si–OH groups in SiOC-H undergo intramolecular reactions to form terminal Si–CH_3 groups. These Si–CH_3 groups decreases the density and dielectric permittivity (from ~8 to 3.55). Annealing induces a transition in the SiOC-H which enhances its etch resistance against diluted hydrofluoric acid solution. We compare the etch selectivity of as-deposited and annealed SiOC-H with that of silicon dioxide during CHF_3/Ar reactive ion etching. Overall, our findings advance the practicality of SiOC-H MLD for fabrication of nanoelectronics.

12:00pm **GWR-MoM-9 From Micro-Batteries to Nano-Ionics: a Two-Decade Journey with Ionic Thin Films***, **Keith Gregorczyk**,* University of Maryland College Park

Keith Gregorczyk completed his PhD under Gary Rubloff in 2013, followed by a postdoctoral fellowship with Mato Knez at CIC nanoGUNE in San Sebastián, Spain. He returned to the University of Maryland as a Research Scientist, where he spent over 15 years — and more than two decades in total working alongside Prof. Gary Rubloff — developing new scientific directions, designing experimental research programs, and mentoring the next generation of graduate students and post docs.

This talk reflects on the scientific journey that emerged from that collaboration: the integration of thin-film ionic materials into semiconductor device architectures using vapor-phase synthesis techniques, particularly atomic layer deposition (ALD). Materials such as $LiPO_3$, LiPON, lithium titanium phosphate (NASICON), and zirconium phosphate introduce new electrochemical functionality — including Faradaic energy storage, electrochromic switching, and non-volatile tunable electronic and ionic conductivities — into platforms traditionally defined by semiconductor design rules. Critically, many of these functional states are low-energy and non-decaying, making them highly attractive for next-generation device integration.

The talk will trace the arc of this work from foundational studies validating the power-energy relationships predicted by Rolison, Dunn, White, and Long in thin-film lithium solid-state batteries, through the development of solid-state sodium-ion systems, to the emergence of a broader framework for advanced nano-ionics: adding electrochemical functionality to solid-state, semiconductor-manufactured devices. This body of work exemplifies the cross-disciplinary spirit that has defined Prof. Rubloff's career — bridging surface science, thin-film synthesis, and electrochemistry to open new frontiers in functional device design.

Author Index

Bold page numbers indicate presenter

— A —
Albertus, Paul: GWR-MoM-6, 1
— D —
Dickey, Michael: GWR-MoM-8, 2
Diebold, Alain: GWR-MoM-2, **1**
— F —
Fontecha, Daniela R.: GWR-MoM-7, **2**
— G —
Ghodssi, Reza: GWR-MoM-3, **1**
Gomez, Osma J.: GWR-MoM-7, 2
Gougousi, Theodosia: GWR-MoM-5, **1**
Gregorczyk, Keith: GWR-MoM-9, **2**
Gregorczyk, Keith E.: GWR-MoM-7, 2
— H —
Hoang, Binh: GWR-MoM-6, 1
— K —
Kim, Nam: GWR-MoM-7, 2
Kim, Seoyeon: GWR-MoM-8, 2
— L —
Lee, Sang Bok: GWR-MoM-7, 2
Lin, Chuan-Fu: GWR-MoM-6, 1
Luo, Xiaolong: GWR-MoM-4, **1**
— P —
Parsons, Gregory: GWR-MoM-8, **2**
— R —
Rubloff, Gary: GWR-MoM-6, 1
Rubloff, Gary W.: GWR-MoM-7, 2
— S —
Song, Yueming: GWR-MoM-6, 1
Stewart, David: GWR-MoM-6, **1**
— T —
Talin, Alec: GWR-MoM-1, **1**
— V —
Vong, Man Hou: GWR-MoM-8, 2