

## Virtual Showcase

### Room Live - Session VS2-WeM

#### How Thin is Thin? Pushing the Limits of Nanoscale Interfacial Engineering

**Moderators:** Mohan Sankaran, University of Illinois at Urbana-Champaign, Scott Walton, Naval Research Laboratory

10:00am **VS2-WeM-1 Welcome to the AVS 67 Virtual Showcase, Mohan Sankaran**, University of Illinois at Urbana-Champaign; *S. Walton*, U.S. Naval Research Laboratory

Welcome to Day 2 of the AVS 67 Virtual Showcase! We hope you will enjoy the session!

10:05am **VS2-WeM-2 Medard W. Welch Award Lecture: Chemically Tailoring Interfaces in Two-Dimensional Heterostructures, Mark Hersam**, Northwestern University **INVITED**

As a result of their unique electronic, optical, and physical properties, two-dimensional (2D) materials are actively being explored for applications in next-generation computing [1], quantum information science [2], and energy technologies [3]. With exceptionally high surface-to-volume ratios, 2D materials are highly sensitive to their environment, resulting in a strong dependence of their properties on substrate effects, extrinsic adsorbates, and interfacial defects. Furthermore, the integration of 2D materials into heterostructure devices introduces further demands for controlling interfaces with atomic precision. With this motivation, this talk will explore emerging efforts to understand and utilize interfacial chemical functionalization to influence the properties of 2D heterostructures. For example, organic adlayers can tailor chemical reactivity to enable conformal atomic layer deposition of pinhole-free encapsulation layers that mitigate the deleterious effects of ambient exposure, particularly for ambient-unstable 2D materials such as black phosphorus and monochalcogenides [4]. The integration of organic self-assembled monolayers with 2D semiconductors also allows for tailoring of electronic and optical properties such as photoinduced charge separation in fullerene/InSe heterojunctions [5] and mixed-dimensional excitonic states in phthalocyanine/MoS<sub>2</sub> heterojunctions [6]. By exploiting spatially inhomogeneous surface chemistry, seamless lateral 2D heterostructures can also be realized including perylene/borophene [7] and graphene/borophene [8] heterostructures, each of which show atomically sharp electronic interfaces as confirmed by ultrahigh vacuum scanning tunneling microscopy and spectroscopy. Overall, by providing substantial tailoring of interfaces, chemical functionalization presents opportunities for improved functionality in 2D heterostructure devices.

[1] V. K. Sangwan, *et al.*, *Nature Nanotechnology*, DOI: 10.1038/s41565-020-0647-z (2020).

[2] X. Liu, *et al.*, *Nature Reviews Materials*, **4**, 669 (2019).

[3] S. Padgaonkar, *et al.*, *Accounts of Chemical Research*, **53**, 763 (2020).

[4] S. A. Wells, *et al.*, *Nano Letters*, **18**, 7876 (2018).

[5] S. Li, *et al.*, *ACS Nano*, **14**, 3509 (2020).

[6] S. H. Amsterdam, *et al.*, *ACS Nano*, **13**, 4183 (2019).

[7] X. Liu, *et al.*, *Science Advances*, **3**, e1602356 (2017).

[8] X. Liu, *et al.*, *Science Advances*, **5**, eaax6444 (2019).

10:55am **VS2-WeM-12 Overcoming Obstacles to Nano-Scale X-ray Tomography of Solid-State Li Battery Electrolytes, Natalie Seitzman**, Colorado School of Mines; *J. Nelson Weker*, SLAC National Accelerator Laboratory; *M. Al-Jassim*, National Renewable Energy Laboratory; *S. Pylypenko*, Colorado School of Mines

Electric vehicles (EVs) significantly reduce carbon emissions over traditional vehicles and, with U.S. market share estimated at 2.1% in 2018, the transition to more environmentally-friendly transportation is already underway.<sup>1</sup> Solid state Li ion conductors are a next-generation battery technology that are particularly promising for EVs. Solid electrolytes offer the capacitive benefits of Li metal anodes while mechanically resisting evolution of the Li interface and thus prolonging lifetime. Additionally, they are not flammable, offering greater safety than liquid counterparts. Despite theoretical mechanical resistance, interface evolution and Li protrusions are empirically observed in solid state batteries and there is debate as to whether these protrusions nucleate at the Li anode or within the ceramic electrolyte.<sup>2,3</sup> Variables that affect these protrusions include interfacial contact, imperfect electronic insulation within the electrolyte, electrolyte density, and pre-existing defects.<sup>3</sup>

This work focuses on investigation of the buried interface between the Li anode and solid electrolyte with the goal of understanding the influence of these variables. X-ray methods are used to directly image the interior of the cells in conjunction with electrochemical measurements. Because many of the pre-existing defects that affect solid-state battery performance are sub-micron, it is necessary to pursue investigation of the interfacial features with nano-scale resolution. Therefore, the contribution of electrolyte density and defects in  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> electrolyte is studied via transmission X-ray microscopy (TXM). This domain is difficult to access via 3D X-ray imaging due to practical limitations, but overcoming these challenges is vital to elucidate Li evolution behavior in realistic systems. A platform for addressing these challenges to achieve nano-scale tomography is presented. Accessing nano-scale evolutions with TXM is also combined with synchrotron micro-tomography to identify sites of Li microstructure growth at the micro-scale.<sup>4</sup> Development of this multi-scale analysis links structural changes observed *in operando* to factors that contribute to Li evolution and will guide the design of robust solid electrolytes with improved performance.

1. R. Irle, *EV-volumes.com* (2019) <http://www.ev-volumes.com/country/usa/>.

2. E. J. Cheng, A. Sharafi, and J. Sakamoto, *Electrochim. Acta*, **223**, 85–91 (2017).

3. F. Han, A. S. Westover, J. Yue, X. Fan, F. Wang, M. Chi, D. N. Leonard, N. J. Dudney, H. Wang, and C. Wang, *Nat. Energy*, **4**, 187–196 (2019).

4. N. Seitzman, H. Guthrey, D. B. Sulas, H. A. S. Platt, M. Al-Jassim, and S. Pylypenko, *J. Electrochem. Soc.*, **165**, 3732–3737 (2018).

11:15am **VS2-WeM-16 Selective Gas-Phase Surface Functionalization to Enable Ultra-High ALE Etch Selectivity of Si-Based Dielectrics, Ryan Gasvoda**, Colorado School of Mines, USA; *Z. Zhang*, *E. Hudson*, Lam Research Corp.; *S. Agarwal*, Colorado School of Mines, USA

Atomic layer etching (ALE) and its derivatives can provide high etch fidelity, atomic-scale precision, directionality, and high selectivity that is required for manufacturing of sub-7-nm node semiconductor devices. Specifically, plasma-assisted ALE of SiO<sub>2</sub> and SiN<sub>x</sub> with ultra-high selectivity for SiO<sub>2</sub> over SiN<sub>x</sub>, and vice versa, is required throughout the manufacturing sequence, especially in self-aligned contact etch pass. Plasma-assisted ALE of SiO<sub>2</sub> and SiN<sub>x</sub> typically consists of two sequential half-cycles: fluorocarbon (CF<sub>x</sub>) deposition from a fluorocarbon plasma followed by an Ar plasma activation step. Generally, process parameters are tuned to maximize overall etch selectivity (similar to continuous etching). Recently, we have identified a novel approach to enhance the overall etch selectivity by selectively pre-functionalizing either the SiN<sub>x</sub> or SiO<sub>2</sub> surface to retard the etch per cycle (EPC).

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy in combination with *in situ* 4-wavelength ellipsometry to monitor surface reactions, film composition as well as etch per cycle during ALE. Further, the ion energy distribution (IED) in the Ar plasma activation half-cycle is characterized with a retarding field energy analyzer. We have previously identified cyclic azasilanes as molecules that can be used to selectively functionalize SiO<sub>2</sub>, and aldehydes as molecules that can be used to selectively functionalize SiN<sub>x</sub> from the gas phase. In particular, benzaldehyde selectively functionalizes only the SiN<sub>x</sub> surface with sp<sup>2</sup>-hybridized-carbon. The net etch of SiN<sub>x</sub> after the first ALE cycle is ~35% less for the benzaldehyde functionalized SiN<sub>x</sub> compared to the bare SiN<sub>x</sub>. Additionally, the infrared spectrum of that benzaldehyde functionalized SiN<sub>x</sub> surface shows more graphitic hydrofluorocarbon film accumulation than the infrared spectrum of the bare SiN<sub>x</sub> surface, indicating that the added sp<sup>2</sup>-hybridized-carbon from benzaldehyde remains on the surface and retards the overall etch. Thus, by pre-functionalizing a SiN<sub>x</sub> surface selective to a SiO<sub>2</sub> surface, overall SiO<sub>2</sub> to SiN<sub>x</sub> etch selectivity can be increased. We will also show that by tuning the surface composition via the hydrocarbon tail of the aldehyde (C:H ratio and hybridization), this etch retardation can be flipped into etch promotion. Further, we discuss the role of maximum ion energy and IEDs in the activation step on overall etch selectivity with specific focus on non-ideal Ar plasma activation steps where the maximum ion energy is above the sputtering threshold of both SiO<sub>2</sub> and SiN<sub>x</sub>.

# Wednesday Morning, October 28, 2020

11:35am **VS2-WeM-20 Sorption and Desorption of TMA During Vapor Phase Infiltration Into Polystyrene and Poly(Methyl Methacrylate) Thin Films**, *Emily McGuinness, C. Leng, M. Losego*, Georgia Institute of Technology, USA

Vapor phase infiltration (VPI) has emerged as a technique for creating hybrid organic-inorganic materials with unique properties. In VPI, vapor phase metalorganic precursors are sorbed and entrapped within the bulk of a polymeric substrate which is then co-reacted with an oxidant generating a metal oxide. To date, VPI has been used to modify industrially relevant properties including the mechanical properties of polymers, stability of polymers in organic solvents, creation of nanoscale features through copolymer patterning, and more. While the utility of VPI has been clearly demonstrated, the fundamental mechanisms of this process remain ill defined. To expedite experimental discovery and industrial application of this process, an improved understanding of the kinetics and thermodynamics of VPI is necessary. In this presentation, we will establish a new theory of metalorganic precursor sorption during VPI. Specifically, we extract fundamental kinetic and thermodynamic values from sorption-desorption curves generated with quartz crystal microgravimetry (QCM) by monitoring metalorganic precursor mass uptake as a function of time and VPI processing step. By exploring the infiltration of polystyrene with trimethylaluminum (TMA) and water, fundamental models for gas sorption in polymers can be applied to a system where no chemical reactions occur with the polymer. By applying models such as the Berens and Hopfenberg model for gas sorption into glassy polymers and Fick's second law, diffusion and relaxation constants and behaviors of polystyrene when exposed to TMA has been quantified. Establishing these behaviors and fundamental values is key to optimizing VPI processes for specific infiltration depths while minimizing reaction times. To further investigate a system where reactions between TMA and the polymer exist, studies of poly(methyl methacrylate) [PMMA] infiltrated with TMA and water, were performed and fundamental models are applied to the system. The TMA/PMMA system exhibits a temperature dependent shift in reaction mechanism which adds complexity to the sorption-desorption process. For this method, a facilitated transport model probes how the strength of the interaction between TMA and the polymer backbone alters the diffusion of TMA throughout the polymer bulk. Overall, by experimentally validating how fundamental polymer theories can be applied to the VPI process, we establish a new framework for interrogating precursor-polymer systems in VPI that results in key thermodynamic and kinetic parameters integral to experimental design and industrial application.

12:05pm **VS2-WeM-26 Emulsion-Templated Asymmetric Vesicles**, *Laura Arriaga*, Universidad Autónoma de Madrid, Spain **INVITED**

A vesicle is a naturally existing or an artificially prepared aqueous droplet stabilized by an amphiphilic membrane that ensures retention of hydrophilic ingredients within its core. This amphiphilic membrane typically comprises two leaflets, which have either identical or different compositions. While membranes comprising two compositionally identical leaflets exhibit lateral asymmetries or domains if prepared from mixtures of amphiphilic molecules capable of phase separation, membranes comprising compositionally different leaflets are asymmetric in the transversal direction. Moreover, internal vesicle asymmetries can be induced through the phase separation of sufficiently concentrated polymer solutions encapsulated in the vesicle cores. All these types of asymmetry dictate vesicle properties, making them more suitable than symmetric vesicles for a wide range of applications, especially to appropriately mimic biological cells. However, the utility of these vesicles depends critically on the degree of control achieved over their properties in the fabrication process. Here, we address the adequacy of emulsion droplets with well-controlled topologies, fabricated with exquisite control by microfluidic technologies, as vesicle templates. In particular, we describe a first strategy to fabricate vesicles with symmetric membranes exhibiting lateral domains and internal asymmetries using double emulsion drops as templates [1,2], and a second strategy to form vesicles with asymmetric membranes using triple emulsion drops as templates [3]. These strategies efficiently encapsulate ingredients within the core of the vesicles or their membranes and yield vesicles with monodisperse sizes and controlled degrees of asymmetry. We are currently exploiting these fabrication strategies to develop vesicles capable of moving on substrates using their interaction with magnetic microparticles that can be actuated with rotating magnetic fields.

[1] L.R. Arriaga, S. Datta, S.-H. Kim, E. Amstad, T. Kodger, F. Monroy, D.A. Weitz. Ultra-thin shell double emulsion templated giant unilamellar lipid vesicles with controlled microdomain formation. *Small* 10, 950-956 (2014).

[2] J. Perrotton, R. Ahijado-Guzman, L.H. Moleiro, B. Tinao, A. Guerrero-Martinez, E. Amstad, F. Monroy, L.R. Arriaga. Microfluidic fabrication of vesicles with hybrid lipid/nanoparticle bilayer membranes. *Soft Matter* 15, 1388-1395 (2019).

[3] L.R. Arriaga, Y. Huang, S.-H. Kim, J.L. Aragones, R. Ziblat, S.A. Koehler, D.A. Weitz. Single-step assembly of asymmetric vesicles. *Lab Chip* 19, 749-756 (2019).

12:35pm **VS2-WeM-32 Atom-Defined Silicon Circuit Elements For Fast, Low Power Computing**, *Robert Walkow*, University of Alberta and The National Institute for Nanotechnology, Canada **INVITED**

CMOS based computers cannot be made substantially more energy efficient or faster. Fast, low power field controlled computing schemes believed capable of reviving Moore's law have not been physically realizable, until now. In such an approach binary information is encoded in spatial charge arrangements among quantum dots. Available quantum dots had been too large, too irregular, and too prone to debilitating charge trap effects. By reducing the quantum dot to a single silicon atom we have made the single electron charging energy very large resulting in dramatically improved noise immunity while also gaining near perfect homogeneity of components and eliminating charge traps. These structures are absolutely stable to over 200 C. And crucially, the silicon atom printing process has been automated and rendered virtually error free.

We will discuss how the atom-scale circuitry works and why it consumes little power ("Binary Atomic Silicon Logic", *Nature Electronics*, 1, 636-643). Atom defined binary wires will be shown. These transmit information extremely rapidly and without the use of conventional current and as a result experience virtually no I<sup>2</sup>R heating. We will also show a working binary logic gate.

The A.I. automated fabrication process and atomic editing will be explained. Also the merging of regular CMOS with atom scale circuitry will be shown. This hybrid CMOS/Atom approach minimizes time to deployment. We can use CMOS circuitry where it is adequate and deploy the atom circuitry as embedded enhancements to reduce power, increase speed, or achieve all-new functions. Three applications will exemplify the advantages of this approach.

1. A neural network simulator will be described that has the potential to deliver Gibbs samples, obviating MCMC sampling when performing unsupervised training on unlabeled data (*Phys. Rev. Lett.*, 121, 166801).
2. The low power prospects of our circuitry are shown by simulating the Google TPU with an atom-defined MXU. Clocking power is reduced 10,000x at 1 GHz. Alternatively, by allowing today's power consumption (limited to 100 W/cm<sup>2</sup> dissipation) clocking of 1 THz becomes achievable.
3. The MXU is for now out of reach because it requires millions of atom printing steps. A practical, ~thousand atom goal is an extremely low power and fast analog to digital converter.

1:05pm **VS2-WeM-38 Closing Remarks & Sponsor Thank Yous**, *Mohan Sankaran*, University of Illinois at Urbana-Champaign

Thank you to everyone for your participation! We hope you enjoyed the Virtual Showcase Session! Please join us tomorrow for another exciting session!

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