

Tuesday Morning, October 27, 2020

Virtual Showcase

Room Live - Session VS1-TuM

It's All in the Details: Mechanistic Understanding of Materials Fabrication and Analysis

Moderators: Mariadriana Creatore, Eindhoven University of Technology, The Netherlands, Dan Killelea, Loyola University Chicago

10:00am **VS1-TuM-1 Welcome Address from the AVS President, Amy V. Walker**, University of Texas at Dallas, USA

The AVS President, Amy V. Walker, welcomes you to the AVS 67 Virtual Showcase. We hope you will enjoy the event!

10:10am **VS1-TuM-3 Welcome Message from the AVS 67 Program Chair, Daniel Killelea**, Loyola University Chicago; **A. Creatore**, Eindhoven University of Technology, The Netherlands, Netherlands

The AVS 67 Program Chair, Dan Killelea welcomes you, thanks all presenters, sponsors, and the community for their support and participation.

10:15am **VS1-TuM-4 Gaede-Langmuir Award Lecture: How Advances in High-Power Magnetron Impulse Sputtering (HiPIMS) Can Control Ion Energy, Ionization, and have High Deposition Rates, David Ruzic**, University of Illinois at Urbana-Champaign **INVITED**

High-Power Magnetron Impulse Sputtering (HiPIMS) is a pulsed physical vapor deposition (PVD) technique which creates a dense plasma near the sputtering target resulting in high ionization of the target material. Normally, most of these ions return to the target and can not be utilized for thin film deposition. However recent advances have changed this picture. The waveform can be altered to provide a short fast negative spike leading to higher energy electrons which cause more ionization. Then, if a positive pulse "kick" immediately follows, the plasma near the target is expelled ionizing even more of the sputtered atoms. Furthermore, by controlling the height and length of the positive kick, the plasma potential is increased. By controlling the magnitude of that plasma potential, the energy of the ions reaching the substrate can be controlled. Further developments allow for additional plasma to be created sustaining the higher plasma potential, and even allowing HiPIMS devices to be used for etching. Deposition rates and ionization fractions can be raised even higher through magnet design. The history of these advances, their underlying physics, and their applications will be presented.

11:05am **VS1-TuM-14 Ru Precursors for Photoassisted Chemical Vapor Deposition: Comparison of Allyl and Diene Complexes, Christopher Brewer**, N. Sheehan, University of Florida; **B. Salazar**, A. Walker, University of Texas at Dallas; **L. McElwee-White**, University of Florida

Chemical vapor deposition (CVD) is a potentially attractive technique for the metallization of organic thin films. However, thermal CVD processes often require high temperatures which are incompatible with organic substrates. Photochemistry provides an alternative means of initiating precursor decomposition without heating the substrate. Readily available Ru precursors, such as (η^3 -allyl)Ru(CO)₃X (X = Cl, Br, I), have been used to deposit Ru on functionalized self-assembled monolayers by means of photochemical CVD as a model system for deposition of metal on a thermally sensitive substrate. Quantum yields for loss of a single CO ligand in alkane solutions were determined for the (η^3 -allyl)Ru(CO)₃X complexes, to elucidate the photochemistry that initiates the deposition process. As a comparative study, the quantum yields for various (diene)Ru(CO)₃ complexes were determined. These (diene)Ru(CO)₃ undergo mixed photolytic decomposition pathways, making them attractive precursors for photochemical CVD. This talk will discuss the photochemistry of the (diene)Ru(CO)₃ complexes relative to the (η^3 -allyl)Ru(CO)₃X complexes with respect to their deposition results.

11:25am **VS1-TuM-18 Rhodium Copper Single-Atom Alloys for Selective and Coke-Free C-H Activation, Ryan Hannagan**, C. Sykes, Tufts University

Due to the recent prevalence of small hydrocarbons, there has been renewed interest in direct dehydrogenation of small alkanes to the corresponding alkenes. One of the major issues in this reaction is the deactivation of catalysts due to coke formation. Here, we report a new RhCu single-atom alloy which displays considerable activity for C-H activation without coke formation. First, using a combination of scanning tunneling microscopy, temperature programmed desorption, and infrared spectroscopy, we characterize the model catalyst surface. We find that Rh atoms exist as isolated sites in the Cu host. We correlate this structure with the binding energy and vibrational frequency of CO on the isolated Rh sites.

With knowledge of the atomic-scale structure, we then examine how the isolated Rh sites promote C-H activation. Using methyl iodide as a reporter on C-H activation, we find the isolated Rh sites promote C-H activation at a significantly lower temperature than Cu(111). We observe the formation of methane (from the hydrogenation of methyl groups) in addition to the formation of ethene (via coupling of CH₂ to CH₃ followed by beta-dehydrogenation). This is in strong contrast to extended Rh ensembles where coke formation is apparent. Together, these results indicate that RhCu single-atom alloys offer significant opportunities for efficient and coke-free C-H activation.

11:45am **VS1-TuM-22 Hydrogen Migration at Restructuring Palladium-Silver Oxide Boundaries Dramatically Enhances Reduction Rate of Silver Oxide, Christopher O'Connor**, Harvard University; **M. van Spronsen**, Lawrence Berkeley National Laboratory (LBNL); **T. Egle**, F. Xu, Harvard University; **H. Kersell**, J. Oliver-Meseguer, Lawrence Berkeley National Laboratory (LBNL); **M. Karatok**, Harvard University; **M. Salmeron**, Lawrence Berkeley National Laboratory (LBNL); **R. Madix**, C. Friend, Harvard University

Heterogeneous catalysts are complex materials with multiple interfaces. A critical proposition in exploiting bifunctionality in alloy catalysts is to achieve surface migration across interfaces separating functionally dissimilar regions. Herein, we demonstrate the enhancement of more than 10⁴ in the rate of molecular hydrogen reduction of a silver surface oxide in the presence of palladium oxide compared to pure silver oxide using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and scanning tunneling microscopy (STM). This enhancement is attributed to the migration of surface species across the palladium-silver interface via hydrogen atoms formed on palladium and oxygen atoms associated with silver. The palladium-silver interface dynamically restructures during oxidation, resulting in palladium dewetting, and during reduction, resulting in silver-palladium intermixing. This study clearly demonstrates the migration of reaction intermediates and catalyst material across surface interfacial boundaries in alloys with a significant effect on surface reactivity, having broad implications for the catalytic function of bimetallic materials.

12:15pm **VS1-TuM-28 Chirality Detection of Surface Desorption Products using Photoelectron Circular Dichroism, J. Wega, Tim Schäfer, G. Westphal**, University Göttingen, Germany **INVITED**

Chirality detection of gas-phase molecules at low concentrations is challenging as the molecular number density is usually too low to perform conventional circular dichroism absorption experiments. In recent years, new spectroscopic methods have been developed to detect

chirality in the gas phase. In particular, the angular distribution of photoelectrons after multiphoton laser ionization of chiral molecules using circularly polarized light is highly sensitive to the enantiomeric form of the ionized molecule (multiphoton photoelectron circular dichroism (MP-PECD)). In the talk, I will present the MP-PECD as an analytic tool for chirality detection of the bicyclic monoterpene fenchone desorbing from a Ag(111) crystal. We recorded velocity resolved kinetics of fenchone desorption on Ag(111) using pulsed molecular beams with ion imaging techniques. In addition, we measured temperature-programmed desorption spectra of the same system. Both experiments indicate weak physisorption of fenchone on Ag(111). We combined both experimental techniques with enantiomer-specific detection by recording MP-PECD of desorbing molecules using photoelectron imaging spectroscopy. We can clearly assign the enantiomeric form of the desorption product fenchone in sub-monolayer concentration. The experiment demonstrates the combination of MP-PECD with surface science experiments, paving the way for enantiomer-specific detection of surface reaction products on heterogeneous catalysts for asymmetric synthesis.

12:45pm **VS1-TuM-34 Thin Film Growth One Step at a Time: Unraveling Mechanisms in Atomic Layer Deposition, Stacey Bent**, Stanford University **INVITED**

With the growing interest in functional nanoscale materials for applications such as electronics, catalysts, and batteries, methods for fabricating materials with atomic-level control are becoming increasingly important. Atomic layer deposition (ALD) is a vapor-based method that provides excellent capabilities for depositing thin solid films, nanoparticles, and other nanoscale materials. Based on sequential, self-limiting vapor-surface reactions, ALD offers exceptional conformality, thickness control at the Angstrom level, and tunable film composition. This talk will describe research into the fundamental processes that drive ALD. Two ALD systems will be presented in which a combination of characterization methods is

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applied to elucidate nucleation and growth mechanisms. In the first system, ALD of binary and ternary metal oxides using ozone as a counterreactant show unusual behavior implicating the importance of trapped reactive oxygen species in these ALD processes. For example, in the growth of ternary Ni-Al-O films using supercycles of nickel oxide and aluminum oxide ALD, Al uptake is greatly enhanced when Al₂O₃ ALD followed a NiO ALD cycle, a result that may arise from the presence of nickel superoxide species after ozone exposure. In ALD of iron oxide by t-butylferrocene and ozone, growth per cycle of greater than one monolayer of Fe₂O₃ per cycle is observed and explained by the presence of excess oxygen stored in the surface regions of deposited films. In the second system, ALD of MoS₂ thin films as well as ALD of metal oxides on MoS₂ will be described. We show that the concentration and size of ZnO nanocrystals grown on MoS₂ by ALD can be independently tuned by controlling the growth conditions. We also introduce a kinetically-driven ALD process for growing stoichiometrically controlled, crystalline MoS₂ from Mo(CO)₆ and H₂S at temperatures as low as 190 °C. Insights into the effect of ALD process conditions on growth behavior and materials properties will be presented.

1:15pm **VS1-TuM-40 Closing Remarks and Sponsor Thank Yous, *Daniel Killelea***, Loyola University Chicago

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

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/MoS₂ 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.¹ 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.^{2,3} Variables that affect these protrusions include interfacial contact, imperfect electronic insulation within the electrolyte, electrolyte density, and pre-existing defects.³

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 β -Li₃PS₄ 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.⁴ 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 SiO₂ and SiN_x with ultra-high selectivity for SiO₂ over SiN_x, and vice versa, is required throughout the manufacturing sequence, especially in self-aligned contact etch pass. Plasma-assisted ALE of SiO₂ and SiN_x typically consists of two sequential half-cycles: fluorocarbon (CF_x) 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_x or SiO₂ 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 SiO₂, and aldehydes as molecules that can be used to selectively functionalize SiN_x from the gas phase. In particular, benzaldehyde selectively functionalizes only the SiN_x surface with sp²-hybridized-carbon. The net etch of SiN_x after the first ALE cycle is ~35% less for the benzaldehyde functionalized SiN_x compared to the bare SiN_x. Additionally, the infrared spectrum of that benzaldehyde functionalized SiN_x surface shows more graphitic hydrofluorocarbon film accumulation than the infrared spectrum of the bare SiN_x surface, indicating that the added sp²-hybridized-carbon from benzaldehyde remains on the surface and retards the overall etch. Thus, by pre-functionalizing a SiN_x surface selective to a SiO₂ surface, overall SiO₂ to SiN_x 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 SiO₂ and SiN_x.

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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 I²R 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/cm² 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!

Virtual Showcase

Room Live - Session VS3-ThM

The Future of the AVS: New Directions, Emergent Materials, and Their Applications

Moderator: Virginia Wheeler, U.S. Naval Research Laboratory

10:00am **VS3-ThM-1 Welcome to the AVS 67 Virtual Showcase, Virginia Wheeler**, U.S. Naval Research Laboratory

Welcome to Day 3 of the AVS 67 Virtual Showcase! We hope you will enjoy the session!

10:05am **VS3-ThM-2 Peter Mark Memorial Award Lecture: Efficient Graphene Hot Electron Devices: Electrochemistry and Electron Emission, Rehan Kapadia**, University of Southern California **INVITED**

In this talk, we will discuss recent work in hot electron devices, focusing on how graphene enables efficient hot electron devices that go beyond the present state of the art in both electron emission and electrochemistry.

First, we show that the onset of electrochemical and photoelectrochemical reactions on a graphene surface can be modified with a semiconductor-insulator-graphene (SIG) device due to injection of hot-electrons from the silicon to the graphene. We observe that the device functions similar to a catalyst, but modifies electrochemical behavior through purely electronic signals. Unlike a material catalyst, such as platinum, which reduces the overpotential at a given current by modifying the transition state energy, the electronic catalyst explored here tunes the onset potential of the reaction by modifying the energy of photoelectrons with respect to the electrochemical reduction energy levels. As a model systems, the hydrogen evolution reaction on graphene is shown to be modified in an n-Si/Al₂O₃/graphene electrochemical device, and a p-Si/Al₂O₃/graphene photoelectrochemical device. Uniquely, it is shown that for every volt of bias applied across the silicon-insulator-graphene junction, the onset of hydrogen reduction on the graphene surface is modified by 1.45 V with a saturation photocurrent density of ~40 mA/cm² indicating nearly ideal minority carrier collection despite the insulator layer.

Next, we show how hot-electron processes can dramatically reduce the optical power densities required for photoemission. In metallic emitters, single-photon, multi-photon, or strong-field emission processes are the three mechanisms via which photoemission takes place. Photons with energy lower than the material workfunction can only drive photoemission through the multi-photon, or strong-field processes, both of which require large optical powers, limiting the integration of photoemitters with photonic integrated circuits. Here, we show that a waveguide integrated graphene electron emitter excited with 3.06 eV photons from a continuous wave (CW) laser exhibits two hot-electron processes that drive photoemission at peak powers >5 orders of magnitude lower than previously reported multi-photon and strong-field metallic photoemitters. Optical power dependent studies combined with modeling illustrate that the observed behavior can be explained by considering direct emission of excited electrons. These processes are dramatically enhanced in graphene due to the relatively weak electron-phonon coupling and the single layer structure. These results show that hot electron devices still offer a rich area of exploration.

10:55am **VS3-ThM-12 The Study of the Effects of Local Environments on Self-Assembled Nanostructures with Tip-Enhanced Raman Spectroscopy, Jeremy Schultz, N. Jiang**, University of Illinois at Chicago

Molecule-substrate interactions are paramount to on-surface chemistry, where highly localized chemical environments determine physical and chemical properties and dynamic processes. Scanning tunneling microscopy (STM) enables the ability to probe individual atoms and molecules, revealing local electronic effects and structure. While tip-enhanced Raman spectroscopy (TERS) combines the rich chemical information available via Raman spectroscopy with the spatial resolution inherent to STM. TERS spectra can reveal the vibrational fingerprint of an individual adsorbate molecule on a surface. This spectral fingerprint is highly sensitive to the observed molecule's local chemical environment, providing the means to thoroughly characterize the effects of molecule-molecule and molecule-substrate interactions. In this work, STM-TERS study of self-assembled domains of rubrene on a Ag(100) surface revealed the ability to unambiguously identify two different binding configurations that result in three unique supramolecular assemblies with angstrom scale spatial resolution We revealed their dependence upon highly localized chemical environment in combination with theory. Furthermore, these unique insights obtained by STM and TERS methods allows us to study the

mechanism of chemical bond formation on noble metal surfaces, such as single atom alloys (Pd/Cu), and ordered anion adlayers. We demonstrate that the role of the local environment, which can determine the selectivity of the products formed, must be fully considered for these surface-bound coupling reactions.

11:15am **VS3-ThM-16 Monolithic Integration of Crystalline III-Vs on Amorphous Substrates using a Combination of Epitaxial and Non-epitaxial Methods, Debarghya Sarkar, R. Kapadia**, University of Southern California

A primary challenge for 3D integration and flexible electronics is the ability to integrate high performance devices at temperatures limited by the thermal budget of the substrate or pre-existing device layers. Present approaches mostly involve hybrid bonding techniques where epitaxial films are first grown on lattice-matched substrates and then transferred to the host substrate at a device scale, circuit scale, chip scale, or wafer scale. Although the devices made using these approaches are of excellent quality, this approach is usually limited by cost, time, limited materials, and scalability perspectives. Monolithic integration approaches attempt to directly grow materials on the host substrate, but device performance is usually poor from solution-based or vapor-phase grown semiconductors on non-epitaxial substrates which give submicron-scale grain polycrystalline films. Here we show results from a liquid-vapor-phase growth approach, referred to as Low Temperature Templated Liquid Phase (LT-TLP) growth. Templates of group III materials capped with SiO₂ are first realized on the non-epitaxial substrate by lithography, evaporation, and liftoff methods. These are then heated in the growth furnace at the intended growth temperature (between 200 to 400 °C), and group V precursor is introduced in the gas phase as pre-cracked V-hydride. The flux of the group V precursor is controlled to ensure single nucleation in each template, which grows with time to yield single crystal III-V in each template, confirmed by electron backscatter diffraction (EBSD) imaging. Photoluminescence measurements for different growth temperatures give an optimal growth window of 280-320 °C, where optoelectronic quality is found to be comparable to single crystal commercial wafer. InAs grown at 300 °C shows room temperature mobility of ~6000 cm²/V-s. Comparing the highest electron mobilities reported from different material families grown directly on amorphous dielectric surfaces, it is seen that TLP III-Vs have the best mobilities, with LT-TLP InAs being about 2 orders of magnitude higher than the majority. These low temperature growths have been performed on rigid dielectric substrates like SiO₂ and HfO₂, as well as on flexible polyimide. Further, these high quality single crystalline mesas have been used as growth seeds for epitaxial films by MOCVD. Growth parameter variations are studied to obtain the best MOCVD InP-on-TLP InP morphology and optoelectronic properties. This potentially opens up a scalable and cost-effective method of integrating high quality III-V materials and devices on inexpensive amorphous dielectric surfaces for 3D integration.

11:35am **VS3-ThM-20 Catalytic Upcycling of Single-Use Polyolefins using Pt Nanoparticles Prepared via Atomic Layer Deposition, Ryan Hackler**, Argonne National Laboratory; *G. Celik*, Middle East Technical University, Turkey; *R. Kennedy*, Argonne National Laboratory; *U. Kanbur*, Ames Laboratory; *A. LaPointe*, *G. Coates*, Cornell University; *K. Poepelmeier*, Northwestern University; *A. Sadow*, Ames Laboratory; *M. Delferro*, Argonne National Laboratory

Modern society relies on synthetic polymers for a variety of applications due to their ease in production, cost, and efficacy. For example, sanitary requirements have made single-use plastics ubiquitous in the medical and food industries. Inefficient and degradable recycling processes, however, have made long-term global management of single-use plastics not viable. As such, our work has focused on transforming polyolefins of varying molecular weight ($M_n = 7.7 - 158$ kDa) and structure (i.e. high- and low-density polyethylene, linear low-density polyethylene, polypropylene) into value-added products through catalytic hydrogenolysis using Pt nanoparticles supported on SrTiO₃ (STO) perovskite nanocuboids. These well-defined Pt nanoparticles are prepared via atomic layer deposition (ALD), and the STO nanocuboids are prepared via hydrothermal synthesis. Regardless of the nature of the starting polymer, waxes and liquids are produced under mild and solvent-free conditions (300 °C, 170 psi H₂, 72 h) with a narrow distribution of molecular weights, a stark contrast to less selective polyolefin conversion processes such as pyrolysis. These value-added waxes and liquids can play an important role in reducing petroleum use and developing a circular carbon economy in the production of lubricants, cosmetics, and chemical intermediates.

Thursday Morning, October 29, 2020

12:05pm **VS3-ThM-26 Atomic-scale Studies of Fe₃O₄(001) and TiO₂(110) Surfaces Following Immersion in CO₂-acidified Water**, *Francesca Mirabella*, Technical University of Vienna, Austria; *J. Balajka*, Cornell University; *J. Pavelec*, *F. Kraushofer*, *M. Schmid*, *G. Parkinson*, *U. Diebold*, Technical University of Vienna, Austria

Atomic-scale studies of mineral dissolution are challenging largely because of the experimental difficulties associated with the integration of liquids into a UHV-based experiment. Recently, we developed a novel experimental setup for the UHV-compatible dosing of ultrapure liquid water, and studied its interaction with TiO₂ and Fe₃O₄ surfaces. Here, we describe a simple approach to vary the pH through the partial pressure of CO₂ (pCO₂) in the surrounding vacuum chamber, and use this to study how these surfaces react to an acidic solution. The TiO₂(110) surface is unaffected by the acidic solution except for a small amount of carbonaceous contamination. The Fe₃O₄(001)-(√2x√2)R45° surface begins to dissolve at a pH 4.0-3.9 (pCO₂ = 0.8–1 bar). Although it is significantly roughened, the atomic-scale structure of the Fe₃O₄(001) surface layer remains visible in scanning tunneling microscopy (STM) images. X-ray photoelectron spectroscopy (XPS) reveals that the surface is chemically reduced, and contains a significant accumulation of bicarbonate (HCO₃⁻) species. These observations are consistent with Fe(II) being extracted by bicarbonate ions, leading to dissolved iron bicarbonate complexes (Fe(HCO₃)₂), which precipitate onto the surface when the water evaporates.

12:25pm **VS3-ThM-30 Light Management Strategies for Photovoltaics: Luminescent Concentrators and Passive Cooling for Modules**, *Vivian Ferry*, University of Minnesota, USA **INVITED**

The solar spectrum is a broad and diffuse light source, but solar panels operate most efficiently at wavelengths near the semiconductor bandgap and over a limited range of incident angles. This talk will discuss different strategies to manage the solar spectrum in photovoltaics: the first part will discuss luminescent solar concentrators that harvest diffuse, high energy sunlight and are integrated into architectural panels, where we use nanostructured luminescent materials and photonic surfaces to enhance performance. The second part will discuss optical strategies to reduce the operating temperature of photovoltaic modules.

Our work on luminescent solar concentrators uses two different nanocrystal luminophores, CdSe/CdS core-shell nanocrystals and Si nanocrystals, embedded into a polymer matrix. These light-emitting nanocrystals offer several advantages over dye molecules, but also exhibit detrimental scattering when aggregated. I will discuss the preparation of nanocrystal-polymer composites with high optical clarity for these applications. The CdSe/CdS nanocrystals are embedded into an alternative polymer, PCHE, and coated into very thin films on glass. The Si nanocrystals are incorporated into PMMA and deposited in thin films via blade coating, and we show that this method results in higher loading fractions than bulk composites. We then apply photonic structures to these luminophore-polymer composites that reduce optical losses and assist in guiding light efficiently toward the edge of the concentrator and onto a small-area solar cell.

The second part will discuss photonic structures for light management in photovoltaic modules. These structures are designed to provide both optical and thermal benefit: they act as broadband and omnidirectional antireflection coatings to improve incoupling of sunlight to the module, while simultaneously reflecting near-infrared light to keep the solar cell operating temperature low. We have developed models that predict energy yield improvement for particular locations, based on typical meteorological year data, and agree with experimental measurements on test modules. We use this model to predict and contrast the performance of mirrors on the outer glass, the surface of the cell, and the rear contact, showing that the mirrors on the glass offer the most temperature reduction. Mirrors on the cell surface, while attractive for reduced weathering, are limited by the textured surface of crystalline Si as well as the optical losses of the encapsulant. To circumvent the multiple reflections at the cell surface, we examine an alternative design consisting of idealized scatterers at the cell interface, and compare the performance of these nanostructures to idealized mirrors.

12:55pm **VS3-ThM-36 Closing Remarks & Sponsor Thank Yous**, *Daniel Killelea*, Loyola University Chicago

Thank you for participating in the AVS 67 Virtual Showcase! We hoped you enjoyed the event and look forward to seeing you in person at AVS 67, October 24-29, 2021, Charlotte, NC!

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