

## 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/Al<sub>2</sub>O<sub>3</sub>/graphene electrochemical device, and a p-Si/Al<sub>2</sub>O<sub>3</sub>/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/cm<sup>2</sup> 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 SiO<sub>2</sub> 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 cm<sup>2</sup>/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 SiO<sub>2</sub> and HfO<sub>2</sub>, 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 SrTiO<sub>3</sub> (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 H<sub>2</sub>, 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 Fe<sub>3</sub>O<sub>4</sub>(001) and TiO<sub>2</sub>(110) Surfaces Following Immersion in CO<sub>2</sub>-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 TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> surfaces. Here, we describe a simple approach to vary the pH through the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in the surrounding vacuum chamber, and use this to study how these surfaces react to an acidic solution. The TiO<sub>2</sub>(110) surface is unaffected by the acidic solution except for a small amount of carbonaceous contamination. The Fe<sub>3</sub>O<sub>4</sub>(001)-(√2x√2)R45° surface begins to dissolve at a pH 4.0-3.9 (pCO<sub>2</sub> = 0.8–1 bar). Although it is significantly roughened, the atomic-scale structure of the Fe<sub>3</sub>O<sub>4</sub>(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 (HCO<sub>3</sub><sup>-</sup>) species. These observations are consistent with Fe(II) being extracted by bicarbonate ions, leading to dissolved iron bicarbonate complexes (Fe(HCO<sub>3</sub>)<sub>2</sub>), 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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