2017 Symposium of the Pacific Northwest Chapter of the AVS

September 7-8, 2017
The LaSells Stewart Center
Oregon State University
875 SW 26th Street
Corvallis, OR 97331

Conference Chair and Vice-Chair
Liney Árnadóttir, Oregon State University
Yingge Du, Pacific Northwest National Laboratory

Program Committee
Scott Smith, Pacific Northwest National Laboratory
Mark Engelhard, Pacific Northwest National Laboratory
Tiffany Kaspar, Pacific Northwest National Laboratory
Shuttha Shutthanandan, Pacific Northwest National Laboratory

Vendor Exibits Coordinator
Joe Gray, Palmborg Associates

Wednesday Workshop organizer:
Gregory S. Herman, Oregon State University

Registration and Badging
Doug Jones and PJ Jones
Welcome to the 2017 PNWAVS Symposium

On behalf of the Pacific Northwest Chapter of the AVS Science and Technology Society (PNWAVS), we warmly welcome you to the 28th Annual Symposium of PNWAVS. We hope that colleagues and friends, together with new arrivals in the field, will find the sessions stimulating and that they will create, renew and deepen acquaintance and collaboration throughout the conference.

About Oregon State University

As Oregon’s leading public research university, Oregon State’s impact reaches across the state and beyond. With 11 colleges, 15 Agricultural Experiment Stations, 35 county Extension offices, the Hatfield Marine Science Center in Newport and OSU-Cascades in Bend, Oregon State has a presence in every one of Oregon’s 36 counties, with a statewide economic footprint of $2.232 billion.

The College of Engineering was founded in 1889, our college endeavors to create solutions that promote strong economies, healthy people, and a sustainable natural environment. Our program has a long history of producing world-class engineering graduates who make major impacts on civilization through significant contributions in science and technology. Alumni achievements include breakthrough innovations such as the first artificial heart valve, the computer mouse, and the concept of email. By emphasizing authentic, experiential engineering experiences within our curriculum, we equip students with the knowledge, skills, and passion to advance innovative solutions to today’s most complex engineering challenges.

2017 PNW-AVS Board

Líney Árnadóttir, Chair
Yingge Du, Vice Chair
Tiffany Kaspar, Secretary
Doug Jones, Treasurer
Joe Gray, Vendor Exhibit Coordinator
Shuttha Shutthanandan, Web Activities and Tutorials
Alex Chang, Western Oregon Representative
Mark Engelhard, Central Washington Representative
Fumio Ohuchi, University of Washington Representative
Jean-Sabin McEwen, Eastern Washington Representative

We are always looking for new members! If you are interested in getting involved, for example as a PNWAVS representative from your school or region, please let one of the Board members know, and join us for our annual Board meeting after the Symposium on Friday.
Vendor Exhibit and Sponsors

We greatly appreciate the support of our sponsors for their generous contributions towards the success of this conference.

<table>
<thead>
<tr>
<th>Company</th>
<th>Representative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agilent Vacuum Products</td>
<td>Ron Neikirk</td>
</tr>
<tr>
<td>Applied Vacuum Tech</td>
<td>Ben Bowers</td>
</tr>
<tr>
<td></td>
<td>Andy Ring</td>
</tr>
<tr>
<td>Busch Vacuum</td>
<td>Jerry Balducci</td>
</tr>
<tr>
<td></td>
<td>Mark Zagorski</td>
</tr>
<tr>
<td>Edwards Vacuum</td>
<td>Joe Gray</td>
</tr>
<tr>
<td>Hiden Analytical</td>
<td>Gerry Duffy</td>
</tr>
<tr>
<td>Inficon</td>
<td>Bill Burnard</td>
</tr>
<tr>
<td>Kurt J Lesker Company</td>
<td>Pierre Hraiz</td>
</tr>
<tr>
<td>MDC Vacuum Product</td>
<td>Tom Bogdan</td>
</tr>
<tr>
<td></td>
<td>Joe Gray</td>
</tr>
<tr>
<td>Nor-Cal Products, Inc.</td>
<td>Nathan Henderson</td>
</tr>
<tr>
<td>ONAMI</td>
<td>Skip Rung</td>
</tr>
<tr>
<td>Oerlikon</td>
<td>Gene Ligman</td>
</tr>
<tr>
<td>Palmborg Assoc, Inc</td>
<td>Joe Gray</td>
</tr>
<tr>
<td></td>
<td>Rod Palmborg</td>
</tr>
<tr>
<td>Physical Electronics, Inc</td>
<td>Saad Alnabulsi</td>
</tr>
<tr>
<td>SAES Group</td>
<td>Russell Graybehl</td>
</tr>
<tr>
<td>SPECS Surface Nano Analysis</td>
<td>Thomas Schumeyer</td>
</tr>
<tr>
<td>Scienta Omicron</td>
<td>Brandon Giles</td>
</tr>
<tr>
<td>SemiTorr, Inc.</td>
<td>Mike Mueller</td>
</tr>
<tr>
<td></td>
<td>Tom Leeland</td>
</tr>
<tr>
<td>Thermo Fisher /FEI Co.</td>
<td>Ted Tessner</td>
</tr>
<tr>
<td>UC Components</td>
<td>Christ Malocsay</td>
</tr>
<tr>
<td></td>
<td>Rich Anderson</td>
</tr>
<tr>
<td>ULVAC</td>
<td>Thomas Simon</td>
</tr>
</tbody>
</table>
Have You Considered Attending the AVS International Symposium & Exhibition?

Each fall, the weeklong AVS International Symposium and Exhibition brings together more than 2,500 attendees from around the globe to:

Engage and Connect - AVS Brings Together a Diverse Community of Scientists and Engineers
Empower Your Career - AVS Provides Professional Growth Activities, Workshops, and Tutorials
Expand Your Knowledge - AVS Delivers the Latest Advances in Materials, Processing and Interfaces

KEY BENEFITS

- **Technical Sessions** – provides the latest advances in the science of materials, surfaces, interfaces, and processing with:
  - 1250+ technical presentations in 15+ parallel oral sessions
  - 2 poster sessions
  - 100+ post-meeting online technical Presentations on Demand

- **Short Courses, Tutorials, and Workshops** – delivers practical training in vacuum and equipment technology; materials and interface characterization; and materials processing

- **Exhibits** – showcases 250+ vendors tools, equipment, services, and publications—plus technology spotlight presentations from exhibitors

- **Networking** – engages professionals from industry, academia, and national labs as well as students at sessions, exhibits, and during social functions like the Welcome Mixer, Awards Ceremony and Reception, and 5k Run

- **Professional Development** – offers insights on fundraising, professional skills, work/life balance—plus opportunities to attend the business meetings and become involved in leadership of AVS chapters, divisions and groups

- **Career Services** – connects job seekers and potential employers at the Career Center—benefit from workshops and other activities including Job Information Forum

- **Awards** – recognizes outstanding scientific research, technological innovation, and leadership at the AVS Awards Ceremony and Reception
Oregon State University Map:

Workshop location:
Johnson Hall 102

PNW-AVS
Conference program
LaSells
Hilton Garden Inn
<table>
<thead>
<tr>
<th>Date</th>
<th>Event</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wednesday, Sept 6th</td>
<td>1:30-5:30 pm Ambient Pressure XPS/STM Workshop</td>
<td>Johnson Hall 102</td>
</tr>
<tr>
<td></td>
<td>5:30-6:30 pm Ambient Pressure XPS/STM laboratory opening reception</td>
<td>Johnson Hall Lobby</td>
</tr>
<tr>
<td>Thursday, Sept 7th</td>
<td>7:40-8:15 am Coffee and Light Refreshments</td>
<td>LaSells Gallery</td>
</tr>
<tr>
<td></td>
<td>8:15-8:20 am Welcome</td>
<td>LaSells, Construction &amp; Engineering hall</td>
</tr>
<tr>
<td></td>
<td>8:20-10:20 am Session I: Surface modification and characterization</td>
<td>LaSells, Construction &amp; Engineering hall</td>
</tr>
<tr>
<td></td>
<td>10:20-10:50 am Coffee Break and Vendor Exhibit</td>
<td>LaSells Gallery</td>
</tr>
<tr>
<td></td>
<td>10:50-12:10 pm Session II: Characterization of surfaces and interfaces</td>
<td>LaSells, Construction &amp; Engineering hall</td>
</tr>
<tr>
<td></td>
<td>12:10-1:10 pm Lunch</td>
<td>LaSells Gallery</td>
</tr>
<tr>
<td></td>
<td>1:10-2:50 pm Session III: In situ and operando studies of surfaces</td>
<td>LaSells, Construction &amp; Engineering hall</td>
</tr>
<tr>
<td></td>
<td>2:50-3:20 pm Coffee Break and Vendor Exhibit</td>
<td>LaSells Gallery</td>
</tr>
<tr>
<td></td>
<td>3:20-4:40 pm Session IV: Synthesis and characterization of thin films</td>
<td>LaSells, Construction &amp; Engineering hall</td>
</tr>
<tr>
<td></td>
<td>4:40-6:30 pm Poster Session/ Vendor Exhibit</td>
<td>LaSells Gallery</td>
</tr>
<tr>
<td></td>
<td>6:30-8:00 pm BBQ dinner</td>
<td>LaSells Gallery/patio</td>
</tr>
<tr>
<td>Friday, Sept 8th</td>
<td>7:30-8:20 am PNW-AVS Board meeting</td>
<td>LaSells Gallery</td>
</tr>
<tr>
<td></td>
<td>7:40-8:20 am Coffee and Light Refreshments</td>
<td>LaSells Gallery</td>
</tr>
<tr>
<td></td>
<td>8:20-10:20 am Session V: Corrosion and Oxidation Mechanism of metals</td>
<td>LaSells, Construction &amp; Engineering hall</td>
</tr>
<tr>
<td></td>
<td>10:20-10:50 am Coffee Break and Awards</td>
<td>LaSells, Construction &amp; Engineering hall</td>
</tr>
<tr>
<td></td>
<td>10:50-12:00 pm Session VI: Surface Physics and electrochemistry</td>
<td>LaSells, Construction &amp; Engineering hall</td>
</tr>
</tbody>
</table>
**Ambient Pressure XPS/STM Workshop**  
Wednesday, September 6th  
Johnson Hall 102  
http://cbee.oregonstate.edu/xps-workshop

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:30-1:35</td>
<td>Liney Arnadottir, Oregon State University</td>
<td>Introduction</td>
</tr>
<tr>
<td>1:35-2:05</td>
<td>Bill Stickle, HP Inc.</td>
<td>XPS tutorial</td>
</tr>
<tr>
<td>2:05-2:35</td>
<td>David Lee, Washington State University</td>
<td>STM tutorial</td>
</tr>
<tr>
<td>2:35-3:05</td>
<td>Brandon Giles, Scienta Omicron</td>
<td>New AP capabilities</td>
</tr>
<tr>
<td>3:05-3:35</td>
<td>Thomas Schulmeyer, SPECS</td>
<td>New AP capabilities</td>
</tr>
<tr>
<td>3:35-4:20</td>
<td>Kelsey Stoerzinger, Pacific Northwest National Laboratory</td>
<td>AP-XPS research</td>
</tr>
<tr>
<td>4:20-5:20</td>
<td>Miquel Salmeron, Lawrence Berkeley National Laboratory</td>
<td>AP-XPS/AP-STM research</td>
</tr>
<tr>
<td>5:20-5:30</td>
<td>Greg Herman, Oregon State University</td>
<td>OSU capabilities and NNCI</td>
</tr>
<tr>
<td>5:30-6:30</td>
<td>Reception</td>
<td>Johnson Hall Lobby</td>
</tr>
<tr>
<td>Invited Speakers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Thursday morning, 8:40 am</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| | Di Wu, Assistant Professor  
Department of Chemical Engineering  
Washington State University |
| **Thursday afternoon, 1:10 pm** |
| | Ethan Crumlin, Research Scientist  
Advanced Light Source |
| **Thursday afternoon, 3:20 pm** |
| | Jason Farmer, Research Scientist  
INTEL |
| **Friday Morning 8:40 am** |
| | Richard Oleksak, Post doctoral Scientist  
NETL |
| **Friday Morning 10:40 am** |
| | David Y. Lee, Assistant Professor  
Department of Chemical Engineering  
Washington State University |
| Time  | Session III: In situ and operando studies of surfaces.  
|-------|-------------------------------------------------------- |
| 1:10pm| Ethan Crumlin ALS  
|       | **Invited:** *In Situ and Operando* Investigations of  
|       | Electrochemical Interfaces Using Ambient Pressure  
|       | XPS  
| 1:50pm| Kelsey Stoerzinger PNNL  
|       | Understanding Photoelectrochemistry on Epitaxial  
|       | Oxides through Surface Electronic Structure  
| 2:10pm| Venkateshkumar Prabhakaran PNNL  
|       | *In-situ* Solid-state Electrochemistry of Precisely-  
|       | defined Electrode-electrolyte Interfaces Prepared  
|       | Using Ion Soft Landing |
### Session IV: Synthesis and characterization of thin films
**Moderator: Tiffany Kaspar PNNL**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:20pm</td>
<td>Jason Farmer</td>
<td>Invited: Process Development at Intel In Pursuit of Moore's Law</td>
</tr>
<tr>
<td>4:00pm</td>
<td>Ryan Frederick</td>
<td>Characterization of Electron and Thermal Induced Behavior of Tin-Based Inorganic EUV Resists in the Presence of Oxygen</td>
</tr>
<tr>
<td>4:20pm</td>
<td>David Bergsman</td>
<td>Mechanisms in the Growth of Ultrathin Organic Films by Molecular Layer Deposition</td>
</tr>
<tr>
<td>4:40pm</td>
<td>Poster Session and Vendor Exhibit</td>
<td></td>
</tr>
<tr>
<td>6:30pm</td>
<td>BBQ Dinner</td>
<td></td>
</tr>
</tbody>
</table>

### Friday, September 8th

### Session V: Corrosion and Oxidation Mechanism on metals
**Moderator: Julie Tucker OSU**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:20am</td>
<td>Audrey K. Taylor</td>
<td>Toward Enhanced Oxygen Evolution Efficiency using Microstructured Nickel Surfaces</td>
</tr>
<tr>
<td>8:40am</td>
<td>Richard Oleksak</td>
<td>Invited: Oxidation Mechanisms of a Ni Alloy in High Temperature CO₂</td>
</tr>
<tr>
<td>9:20am</td>
<td>Lucas Teeter</td>
<td>Environmentally Induced Cracking of Energy System Materials in Supercritical Carbon Dioxide</td>
</tr>
<tr>
<td>9:40am</td>
<td>Hossein DorMohammadi</td>
<td>Reactive molecular dynamics modeling of classical models of iron/electrolyte interface</td>
</tr>
<tr>
<td>10:00am</td>
<td>Qin Pang</td>
<td>Effects of Surface Defects on the Interactions of Cl and α-Fe₂O₃ (0001) Surface: A Density Functional Theory Study</td>
</tr>
<tr>
<td>10:20am</td>
<td>Coffee Break and Awards</td>
<td></td>
</tr>
</tbody>
</table>

### Session VI: Surface Physics and electrochemistry
**Moderator: Greg Herman OSU**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:40am</td>
<td>David Lee</td>
<td>Invited: Radical-Induced Topography and Physical Property Modifications on Materials Surfaces</td>
</tr>
<tr>
<td>11:20am</td>
<td>Arjun Dahal</td>
<td>Formation of Metastable Water Chains on Anatase TiO₂(101)</td>
</tr>
<tr>
<td>11:40am</td>
<td>Yanyan Zhang</td>
<td>In situ Molecular Verification of Ethanol Electrocatalysis Mechanism at Polycrystalline Gold Electrode Surfaces</td>
</tr>
<tr>
<td>#</td>
<td>Presenter</td>
<td>Title</td>
</tr>
<tr>
<td>----</td>
<td>-----------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>G1</td>
<td>Qin-qin Yuan</td>
<td>Probing anion and molecular specificities using electrospray ionization photoelectron spectroscopy</td>
</tr>
<tr>
<td>G2</td>
<td>Xiaofei Yu</td>
<td>An Overview of In situ Liquid Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>G3</td>
<td>Yujuan He</td>
<td>Optically Transparent Glass from Microfluidic-assisted Sol-Gel 3D-Print</td>
</tr>
<tr>
<td>G4</td>
<td>James Elliott Fowler</td>
<td>Coming Together Under Pressure: Using Surface Analytical Tools to Dissect the Role of Fibril Formation in the Frog Sticky-Tongue Mechanism</td>
</tr>
<tr>
<td>G5</td>
<td>Benjamin Taber</td>
<td>Particles in Organic Boxes: Scanning Tunneling Spectroscopy of Molecular Electronic Structure</td>
</tr>
<tr>
<td>G6</td>
<td>Stebby Varghese</td>
<td>Dissolution and Electrical Stability Studies of Functionalized Indium-Gallium-Zinc Oxide Field Effect Sensors</td>
</tr>
<tr>
<td>G7</td>
<td>John Trey Diulus</td>
<td>Ambient pressure X-ray photoelectron spectroscopy investigation of radiation induced chemistries of organotin clusters</td>
</tr>
<tr>
<td>G8</td>
<td>Kofi Oware Sarfo</td>
<td>Theoretical study of γ-Al₂O₃ surface and interface with Pt(111) via Density Functional Theory</td>
</tr>
<tr>
<td>G9</td>
<td>Yujing Zhang</td>
<td>Localized Surface Plasmon Resonance Enhanced Carbon Dioxide Gas Sensing based on Nanostructured Copper Sulfide Thin Films</td>
</tr>
<tr>
<td>G10</td>
<td>Weinan Zhao</td>
<td>Density Functional Theory Study of CO₂ dissociation of Ni(111) surface</td>
</tr>
<tr>
<td>G11</td>
<td>Maoyu Wang</td>
<td>In Situ Observation of Catalyst Reconstruction During Electrochemical CO₂ Reduction</td>
</tr>
<tr>
<td>G12</td>
<td>Zhongwei Gao</td>
<td>Scalable fabrication of patterned ZnO nanostructures by using microreactor-assisted nanoparticle deposition process and microfluidic channels</td>
</tr>
<tr>
<td>G13</td>
<td>Han Mei</td>
<td>Long silver nanowire synthesis and its application</td>
</tr>
<tr>
<td>G14</td>
<td>Okan Agirseven</td>
<td>Determination of Amorphous Precursors Under Various Deposition Pressures and Their Effects on the Crystalline Phase Distribution of TiO₂ Thin Films Deposited by Pulsed Laser Deposition</td>
</tr>
</tbody>
</table>
### Contributed Posters

<table>
<thead>
<tr>
<th>#</th>
<th>Presenter</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Zheng Yang</td>
<td>Structures, Energetics and Interactions of Aerosol Related Species and Clusters</td>
</tr>
<tr>
<td>C2</td>
<td>Juan Yao</td>
<td>In situ Characterization of Switchable Ionic Liquids by Liquid ToF-SIMS and SALVI</td>
</tr>
<tr>
<td>C3</td>
<td>Phuong-Vu Ong</td>
<td>Structure and defects at grain boundaries in cathode material LiCoO₂: A first-principles study</td>
</tr>
</tbody>
</table>

### Undergraduate Student Poster Competition

<table>
<thead>
<tr>
<th>#</th>
<th>Presenter</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>Cassandra Leah Remple</td>
<td>Growth Kinetics of ZnS Thin Films from a High-Rate Chemical Bath Deposition with Trisodium-nitritriacetate Complexing</td>
</tr>
<tr>
<td>U2</td>
<td>Konner Holden</td>
<td>High-Voltage Nanolaminate Metal-Insulator-Insulator-metal (MIIM) Tunnel Diodes using ADL Al₂O₃ and Ta₂O₅</td>
</tr>
<tr>
<td>U3</td>
<td>Daniel Goddard</td>
<td>Binding Behavior of Butyl-tin β-Keggin Resists on Mica Substrate</td>
</tr>
<tr>
<td>U4</td>
<td>Joseph Hebert</td>
<td>Adsorption of Butyl-tin β-Keggin Clusters on HOPG Substrate</td>
</tr>
<tr>
<td>U5</td>
<td>David Catherall</td>
<td>Micro-reactor assisted deposition of patterned CuO thin film for the enhancement of condensation</td>
</tr>
</tbody>
</table>
Presentation Abstracts

2017 Symposium of the Pacific Northwest Chapter of the AVS

September 7-8 2017
The LaSells Stewart Center at
Oregon State University
875 SW 26th Street
Corvallis, OR 97331
The proton solvation and transfer plays an essential role for fundamental material science, chemical, electrochemical and biochemical process. Although numerous studies has been presented and great progress has been made in this realm, however, the direct evidence for the dynamics of the hydrated protons near the electrode-electrolyte interface during the electrochemical reaction, which are key to the understanding of proton transfer in the proton coupled electrochemical process, have remained experimentally elusive thus far. Recently, in situ liquid SIMS coupled with electrochemistry has been developed to molecularly examine intermediates of redox reactions and formation mechanism of the solid electrolyte interphase in lithium-ion batteries. Here, the electrochemical oxidation of acetaminophen was chosen as a model system to study proton transfer, which simulated the function of oxidase enzymes cytochrome P-450 to catalyze the oxidation of acetaminophen. The highly reactive N-acetyl-p-benzoquinone-imine (NAPQI) was captured. Most importantly, this work provides the direct molecular evidence for the hydration of protons and transport during the electrochemical reaction which cannot be obtained using any traditional electrochemical approaches. These results demonstrate that the coupling of in situ liquid SIMS and electrochemistry is a powerful approach to molecularly elucidate reaction machinisms in the oxidative metabolism and reveal ions dynamics at electrode-electrolyte interface under polarized condition.

References
Invited talk: Probing the Heterogeneity of Material Surfaces using Calorimetry

Di Wu
The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Department of Chemistry, and Materials Science and Engineering, Washington State University, Pullman, Washington 99163, United States

During the last few years, we focused on probing the energetics of molecule–material interactions using various calorimetric techniques. Here, I present a few systems, which have been or are being studied. Materials (adsorbent or host) investigated include metal–organic frameworks (MOFs), zeolites, mesoporous materials, nanoparticles, and inorganic oxide heterogeneous catalysts. The surface heterogeneity of these materials can be directly reflected by the thermochemical data recorded. Molecules (adsorbate or guest) introduced range from water, carbon dioxide, and methane to simple organics. These molecules are usually seen in the Earth’s critical zone and at engineering conditions, and are of great significance in interfacial phenomena encountered in geochemical evolution, material formation, and chemical catalysis processes.
Soft-Landing and Reactive Binding of Ru Clusters to Ca(NH$_2$)$_2$: Effect of Hydrogen and Electron Transfer

Phuong-Vu Ong,$^1$ Hideo Hosono,$^2$ and Peter V. Sushko$^1$

$^1$Physical Sciences Division, Physical & Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, U.S.A.

$^2$Materials Research Center of Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8053, Japan

Search for an efficient and stable catalyst enabling ammonia synthesis under mild conditions is a major topic in catalysis research. Recent experimental studies [1] demonstrated that flat Ru nanoparticles on calcium amide [Ca(NH$_2$)$_2$] enable continuous synthesis of NH$_3$ at temperatures as low as $\sim$200 °C and ambient pressure. In order to extend these results to a broader class of catalysts, we aim to understand the atomistic origin of this low-temperature activity and to reveal effects specific to the supporting surface and the size and shape of Ru nanoparticles. In this work, we investigate thermodynamic stability of Ca(NH$_2$)$_2$ surfaces in different crystallographic orientations and interactions of small Ru clusters and flat nanoparticles with the amide support using ab initio simulations. It is shown that NH$_2^-$ anions reorient and/or donate protons to facilitate the formation of N-Ru bonds and, thus, anchor the nanoparticles. Formation of a precursor layer by Ru adsorption at hollow sites is also found to promote a two-dimensional growth of Ru nanoparticles. We found that NH$_2$ vacancy state is very shallow. We propose that these effects enhance reduction of dinitrogen on the nanoparticles and hence render them catalytically active.

Surface Modifications on LiCoO$_2$-Based Cathodes for High-Density Lithium-Ion Batteries with Long Cycle Life

Wentao Wang,$^1$ Arni Sturluson,$^1$ Zelang Jian,$^1$ Yige Wang,$^1$ Nick AuYeung,$^1$ Zhenxing Feng,$^1,^*$

$^1$School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, Oregon, 97331, United States

*E-mail: zhenxing.feng@oregonstate.edu

Commercial rechargeable lithium-ion batteries (LIBs) use LiCoO$_2$ (LCO) as the cathode, which shows relatively low energy capacity (≈140 mAh/g) and suffers poor cycle life performance. To develop next-generation LIBs with high capacity and long cycle life, surface modifications on cathodes have been applied. We use thin layers of Al$_2$O$_3$ synthesized from sol-gel method to coat on the LCO surfaces and to test the optimal conditions, namely thickness and annealing temperature, for LIB performances in both half-cell and full cell configurations. Although high temperature annealing, i.e., >1100 °C, can help form crystalline $\alpha$-Al$_2$O$_3$, 600°C is found to be the right temperature for achieving the most improved battery performance compared to pure LCO cathode. After identifying the best thickness for surface coating, we are moving to test new types of Li$^+$ conducting surface coating as predicted by density functional theory on LCO-based cathodes for high-density LIBs with long cycle life.
Structural and chemical evolution of thin film LiCoO₂ electrodes observed by \textit{in situ} TEM

Zhenzhong Yang\textsuperscript{1}; Timothy C Droubay\textsuperscript{1}; Mark Bowden\textsuperscript{2}; Mark Engelhard\textsuperscript{2}; Zhenxing Feng\textsuperscript{3}; Le Wang\textsuperscript{1}; Yingge Du\textsuperscript{1}.

\textsuperscript{1}Physical & Computational Sciences Directorate and \textsuperscript{2}Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory Richland, WA 99352, United States
\textsuperscript{3}Oregon State University, Corvallis, OR, United States.

Email: Zhenzhong.Yang@pnnl.gov; Yingge.Du@pnnl.gov

Lithium cobalt oxide (LiCoO₂, LCO) is one of the most extensively studied/used cathode materials for rechargeable lithium ion batteries. Well-defined, single crystalline LiCoO₂ thin films and multilayered structures are highly desirable for fundamental investigations of the charge/discharge processes. In our work, epitaxial LiCoO₂ thin films with different orientations and strain states were grown by pulsed laser deposition (PLD). Fig.1 shows an example of the interface structure between a 150 nm LiCoO₂ and a 10 nm SrRuO₃ buffer layer grown on an STO(111) substrate. All-solid-state thin film battery was constructed under scanning transmission electron microscopy (STEM) in combination with oxide electrolyte and metallic Li contact. \textit{In situ} (S)TEM was employed to investigate the structural and chemical evolution of the constructed LCO thin film electrode during delithiation/lithiation. EELS, EDX, and NBD were used to study the reaction product, lithium diffusion pathways, and intercalation induced phase changes, in particular occurring at the interfaces. These results will be compared to electrochemical cycling performance measured with traditional techniques to establish connections between atomic-level structure evolution and microscopic change in electrochemical characteristics.

Fig.1 HAADF image of LiCoO₂ thin film grown on STO(111) substrate with SrRuO₃ buffer layer.
Determination of Energy Barrier Heights of ALD and Solution Deposited Dielectrics using Internal Photoemission Spectroscopy

M.A. Jenkins, 1 T. Klarr, 1 C.K. Perkins, 2 T.-H. Chiang, 1 J. McGlone, 1 J.F. Wager, 1 D.A. Keszler, 2 and J.F. Conley, Jr. 1  
1School of Electrical Engineering and Computer Science, Oregon State University Corvallis, Oregon 97330  
2Department of Chemistry, Oregon State University, Corvallis, OR, 97330

High quality insulators are an enabling technology for thin film metal-insulator-metal (MIM) tunnel diodes. 1,2 Operation of these devices is ideally based on Fowler-Nordheim tunneling, which is exponentially dependent on both the thickness of the insulator and the height of the energy barriers between the metal electrodes and the insulator. Accordingly, smooth bottom electrodes and precise knowledge of metal/insulator barrier heights are critical for predicting, understanding, and optimizing MIM diode device operation. Although ideal barrier heights may be predicted from measurement of individual materials, actual barrier heights depend strongly on deposition method and interfacial properties and often deviate substantially from the ideal Schottky-Mott model of the difference between metal vacuum work function and insulator electron affinity. Therefore it is necessary to directly measure the barriers of interest.

While atomic layer deposition (ALD) films are an industry standard for high-quality films, solution deposited (SD) films show promise for MIM devices and offer the benefit of atmospheric pressure deposition. 3 In this work, we use internal photoemission (IPE) spectroscopy to measure the barrier heights for several ALD insulators and a SD insulator in MIM structures with TaN or amorphous metal bottom electrodes and Au or Al top electrodes. The built-in field polarity, determined from IPE, agreed with asymmetry from current-voltage measurements for ALD devices. However, the barrier heights extracted from IPE (Fig. 1) differed from ideal values in a number of cases, owing either to the presence of an interfacial oxide or charge in the insulator. Detailed discussion of the results will be given at the meeting. Support from NSF Center for Sustainable Materials Chemistry, CHE-1606982.


![Figure 1. Extracted barrier heights for ALD insulators on amorphous metal TaWSi electrodes with Al top contacts.](image-url)
Phase transitions and resistive switching in epitaxial SrFeO$_{3-\delta}$ thin films

Le Wang$^1$, Mark E Bowden$^2$, Zhenzhong Yang$^1$, Steven R Spurgeon$^1$, Martin E McBriarty$^1$, Yingge Du$^1$

$^1$Physical and Computational Sciences Directorate, PNNL
$^2$Environmental molecular sciences laboratory, PNNL

Strontium ferrite SrFeO$_{3-\delta}$ (SFO) has recently been studied extensively in the field of technological applications such as fuel cells, oxygen sensors, magnetic storage and catalysts. Depending on its oxygen stoichiometry, the crystal structure of SFO exhibits a topotactic phase transformation from perovskite (P), brownmillerite (BM) to infinite layer structure. Here, we report on the epitaxial growth of high quality BM-SFO thin films on (001)-oriented SrTiO$_3$ (STO) and Nb-doped SrTiO$_3$ (Nb-STO) substrates by using MBE. Topotactic phase transformation from BM-SFO to P-SFO can be realized by annealing the sample in air at 600ºC for one hour. XRD measurements reveal that the BM-SFO phase prefers to grow as c-axis-oriented on STO substrate. Topotactic phase transition from BM to P-phase can be realized by post-annealing. XPS measurements confirmed the phase transition from BM-phase to P-phase changed the electronic structure. The local transport properties of the BM-SFO films were measured with conductive atomic force microscopy (C-AFM) by using the Nb-STO as the bottom electrode. Interesting resistive switching phenomenon has been observed in BM-SFO films. Repeated measurements at the same point and other locations confirmed that this resistive switching behavior is reliable. The SFO/Nb-STO interface should play an important role in the observed resistive switching. The oxygen ions movement driven by electric field induced the phase transition between BM-SFO and P-SFO would be the origin of the observed resistive switching. Further measurements and theoretical calculation results are ongoing.
TiO2/SiOx bilayer insulating stacks with filamentary/distributed resistive switching behavior

Bingru Wang1, Na Xiao1, Marco A. Villena1, Bin Yuan1, Shaochuan Chen1, Marek Eliáš2, Yuanyuan Shi1,4, Fei Hui1,3, Xu Jing1, Andrew Scheuerman5, Kechao Tang5, Paul C. McIntyre5 and Mario Lanza1*

1 Institute of Functional Nano & Soft Material (FUNSOM), NANO-CIC, Soochow University, 199 Ren-Ai Road, Industrial Park, Suzhou, 215123, China
2 CEITEC BUT, Brno University of Technology, Brno 61669, Czech Republic
3 Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
4 Department of Electrical Engineering, Stanford University, California 94305, USA
5 Department of Materials Science and Engineering, Stanford University, California 94305, USA

* Corresponding author. Email: mlanza@suda.edu.cn - Group website: www.Lanzalab.com

Resistive random access memories (RRAM) have been raised as one of the most promising technologies for future information storage due to their excellent performance and easy fabrication in the past few years. In this work we present a new strategy for extending the performance of RRAMs only using cheap and industry-friendly materials which can show filamentary and distributed resistive switching (RS) simultaneously (i.e. in the same I-V curve) (Fig. 1) by Ti/TiO2/SiOx/n++Si cells. It exhibited unprecedented hysteretic I-V characteristics, high current on/off ratios up to approximately 5 orders of magnitude, good cycle-to-cycle endurance (>1000 cycles) and low device-to-device variability of the devices. This behavior can be proved by Quantum Point Contact (QPC) and Poole-Frenkel’s theory. We are not aware of any other resistive switching memory exhibiting such characteristics, which may open the door for the development of advanced NVMs combining the advantages of filamentary and distributed resistive switching mechanisms.

Figure 1: (a)-(b) Typical I-V characteristics exhibited by RRAMs working under filamentary and distributing switching mechanisms (respectively). (c) Typical I-V characteristics exhibited by the RRAM cells fabricated in this work, which combine both filamentary and distributed conduction mechanisms. Curve thick arrows to indicate the abrupt set/reset event typical of filamentary RS, and thin straight arrows to indicate progressive transitions typical of distributed RS. The schematics in the bottom row display the conduction mechanism in each device.
Exploration of the Site-Pairing Preference of Framework Aluminum in ZSM-5 from its Reaction with Ga(CH3)3

Kyle Groden\textsuperscript{a}, Renqin Zhang\textsuperscript{a}, Susannah Scott\textsuperscript{b}, Jean-Sabin McEwen\textsuperscript{a}

\textsuperscript{a} Washington State University, WA, 99164;
\textsuperscript{b} University of California, Santa Barbara, CA, 93106;

ZSM-5 is a zeolite catalyst marked with great versatility in catalytic application as a result of its flexibility in cation incorporation. Due to this property, the structure of ZSM-5 has been under question for its ability to accept divalent cations, implying that the substituted aluminum sites exist in paired configurations at specific locations within the zeolite framework. Trimethylgallium was used to probe these sites, as the dimethyl gallium fragments that exist in these locations following impregnation were thought to bind to nearby fragments via terminal methyl groups. Experimental extended x-ray absorption fine structure (EXAFS) spectroscopy data supports this “bridging” configuration due to the presence of potential gallium-gallium scattering signals. Zeolite cluster models were created containing potential sites for aluminum pairings with dimethyl gallium fragments, with optimized geometrical conformations obtained from first principles calculations based on density functional theory (DFT) implemented in the VASP program.\textsuperscript{1,2} As methyl-bridged structures were unfavorable, additional cluster and periodic models were constructed to explore the possibility of carbon-hydrogen bond cleavage due to the reactivity of the methyl groups bound to the gallium centers. This reaction results in a methylene (CH\textsubscript{2}) group joining the gallium centers in contrast with the methyl bridges previously hypothesized. X-ray absorption near edge spectra (XANES) were computed using CASTEP\textsuperscript{3}, another DFT program, for many of these configurations examined, which allows for a direct comparison with the synchrotron-based experimental results. The agreement between the gallium-gallium bond distances and spectral results from our calculations and those measured experimentally imply that paired aluminum sites are indeed present within the ZSM-5 architecture.

Invited talk:

_In Situ and Operando_ Investigations of Electrochemical Interfaces Using Ambient Pressure XPS

Ethan J. Crumlin
 ejcrumlin@lbl.gov

Interfaces play an important role in nearly all aspects of life, and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. The ability to study these interfaces has proven to be difficult and is only further exacerbated by the limited number of techniques capable of operating under _in situ/operando_ environments. To overcome these challenges, we use _in situ/operando_ ambient pressure X-ray Photoelectron Spectroscopy (APXPS). APXPS is a photon-in/electron-out process that can provide both atomic concentration and chemical specific information at pressures greater than 20 Torr. Using synchrotron X-rays at Lawrence Berkeley Nation Laboratory, the Advanced Light Source has several beamlines dedicated to APXPS endstations that are outfitted with various _in situ/operando_ features such as heating to temperatures > 500 °C, pressures greater than 20 Torr to support solid/liquid experiments and electrical leads to support applying electrical potentials supports the ability to collect XPS data of actual electrochemical devices while its operating in near ambient pressures. This seminar will introduce this technique and provide several solid/gas and solid/liquid interface electrochemistry examples using _operando_ APXPS including SOFC, solid-state Li-air batteries, electrochemical stripping, water splitting, and the ability to probe the electrochemical double layer (EDL). Gaining new insight to guide the design and control of future electrochemical interfaces.
Understanding Photoelectrochemistry on Epitaxial Oxides through Surface Electronic Structure

Kelsey A. Stoerzinger¹, Yingge Du¹, Scott A. Chambers¹
¹Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland WA 99352, United States

The intermittent nature of renewable energy sources requires a clean, scalable means of converting and storing energy. One earth abundant storage option is water electrolysis, storing energy in the bonds of O₂ and H₂. Photoelectrochemical (PEC) cells based on semiconductor/liquid interfaces can convert sunlight to chemical fuels by “splitting” water into O₂ and H₂ upon illumination of a photoabsorber and catalyst. The efficacy of conversion depends in part on the rectifying properties of semiconductor–electrolyte junctions, as the band bending present in the semiconductor space-charge region from Fermi level equilibration drives the separation of electron–hole pairs. However, the relationship between band structure, band bending/flattening, photocatalytic activity, and surface functionality (such as hydroxylation properties and hydrophilicity) is not well understood.

In the particular case of the semiconductor Ge, favorable conduction band alignment with the hydrogen evolution reaction (HER) suggests the potential for efficient solar-to-hydrogen conversion with visible light. However, material instability in aqueous environments and the potential for photocorrosion limits its utility in PEC applications. In order to protect the photoabsorber surface while maintaining favorable alignment of the conduction band, we epitaxially grow SrTiO₃ on top of p-Ge. We will present studies of such model oxide photoelectrodes grown by molecular beam epitaxy (MBE) on single crystal substrates that display a known crystallographic orientation, surface area, path for charge transport, and strain. Photoelectrochemical measurements on these heterostructures can establish the intrinsic activity of oxide catalysts in a way that cannot be realized with polydisperse nanoparticle systems. Insight into the band bending between the substrate and oxide overlayer, as well as at the semiconductor surface, can be obtained from X-ray photoelectron spectroscopy (XPS). Measurement of XPS at ambient pressures (AP-XPS) can further elucidate the relationship between adsorbates and surface band bending. This fundamental insight will build understanding necessary for the design of active, earth-abundant photocatalysts that can be integrated into PEC devices for efficient conversion of solar energy into chemical fuels.
In-situ Solid-state Electrochemistry of Precisely-defined Electrode-electrolyte Interfaces Prepared Using Ion Soft Landing

Venkateshkumar Prabhakaran, Grant E. Johnson and Julia Laskin
Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352.

Molecular-level understanding of electrochemical processes occurring at electrode-electrolyte interfaces (EEI) is key to the rational development of high-performance electrochemical technologies such as batteries, supercapacitors, and fuel cells. Soft landing of mass-selected ions is ideally suited for controlled preparation of well-defined surfaces that provide detailed insights into processes at EEI. Specifically, ion soft landing enables deposition of uniform layers of redox-active species onto electrodes with precise control over charge state, composition, coverage and kinetic energy. Herein, we report the development and first demonstration of the capabilities of an in-situ solid-state three electrode electrochemical cell designed to study the electrochemical activity of mass- and charge- selected ionic clusters deposited onto electrode surfaces using ion soft landing. Specifically, we examined the intrinsic redox activity of mixed-addenda Keggin PMoₓW₁₂₋ₓO₄₀³⁻ (x=0,1,2,3,6,9,12) polyoxometalates in a clean vacuum environment. The multi-electron redox activity of stable anionic Keggin POMs enables transfer of up to 24 electrons per cluster while retaining their structure which makes them attractive systems for incorporation into advanced catalytic and energy storage materials. In addition, we examined the catalytic oxygen reduction reactivity of bare Pt cluster ions ~1 nm in diameter produced using magnetron sputtering combined with gas aggregation. Soft landing of bare metal cluster ions directly onto the cell eliminates the need to use stabilizing ligands or solvent and, therefore, provides a direct route for studying intrinsic electrocatalytic activity at controlled reactive gas conditions. In summary, the newly designed in-situ electrochemical cell combined with mass-selected ion deposition is shown to be a powerful approach for studying processes both at model and technologically-relevant EEIs during operating conditions.
Proteins that contain C2 domains are involved in a variety of biological processes including encoding of sound, cell signaling, and cell membrane repair. Of particular importance is the interface activity of the C-terminal C2F domain of otoferlin due to the pathological mutations known to significantly disrupt the protein’s lipid membrane interface binding activity, resulting in hearing loss. Therefore, there is a critical need to define the geometry and positions of functionally important sites and structures at the otoferlin-lipid membrane interface. Here we describe the first in situ probe of the protein structure of otoferlin’s C2F domain interacting with a cell membrane surface. To identify this protein’s structure at the lipid interface we applied sum frequency generation (SFG) vibrational spectroscopy and coupled it with simulated SFG spectra to observe and quantify the otoferlin C2F domain interacting with model lipid membranes. A model cell membrane was built with equal amounts of phosphoserine (PS) and phosphocholine (PC). SFG studies that examined the ordering of the lipids that make up the model membrane, demonstrate that lipid fusion occurs after docking of the otoferlin C2F domain via the observation of a 62% increase in amplitude from the SFG signal near 2075 cm\(^{-1}\) assigned to specific groups within the model membrane. This increase is related to lipid ordering caused by the docking interaction of the otoferlin C2F domain. SFG spectra taken from the amide I region contain peaks near 1621 cm\(^{-1}\) and 1672 cm\(^{-1}\) related to the C2F domains beta-sandwich secondary structure, thus, indicating that the domain binds in a specific orientation. By mapping the simulated SFG spectra to the experimentally collect SFG spectra, we found the C2F domain of otoferlin orients 32° normal to the lipid surface. This information allows us to map what portion of the domain directly interacts with the lipid membrane. Furthermore, we show first experimental view of any C2 domain of otoferlin docked at the membrane interface, thereby, validating SFG as a method to probe C2 domain-membrane interfaces.
Invited talk:

Process Development at Intel In Pursuit of Moore's Law

Jason Farmer

Intel Corporation, Hillsboro Oregon

Dr. Jason Farmer is a process engineer in the metals deposition group at Intel corporation in the Portland technology development department. In 2010 he received his PhD from University of Washington in physical chemistry (UHV surface science). He has been at Intel since 2010 developing metals deposition processes to enable continued semiconductor device scaling. His talk will review device scaling at Intel, the barriers to continued scaling, and how we engineer or invent our way around the barriers to scaling.
Characterization of Electron and Thermal Induced Behavior of Tin-Based Inorganic EUV Resists in the Presence of Oxygen

R.T. Frederick¹, J.T. Diulus¹, D. C. Hutchison², M.R. Olsen², M. Li³, E.L. Garfunkel³, M. Nyman², G.S. Herman¹²

¹ School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR, 97331, USA
² Department of Chemistry, Oregon State University, Corvallis, OR, 97331, USA
³ Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, USA

The transformation to the 7-nm generation of microelectronics process technologies requires higher pattern resolution which is enabled by a decrease in photon wavelength by the transition to extreme ultraviolet (EUV) radiation (λ = 13.5 nm) from deep ultraviolet (DUV) radiation (λ = 193 nm). This transition requires the development of new photoresist materials with high EUV photoabsorption cross sections. One promising system is organotin compounds since tin atoms have ~30x higher EUV absorption cross section compared to carbon atoms. To better understand radiation induced chemistries we have studied NaO₄(BuSn)₁₂(OH)₃(O)₉(OCH₃)₁₂(Sn(H₂O)₂) (β-NaSn₁₃), which is a charge-neutral, model EUV photoresist material. The β-NaSn₁₃ clusters are small and uniform, which allows for high resolution patterning with low line edge roughness. The relatively weak tin-carbon bond provides a mechanism for radiation induced modification of the cluster chemistries. We have used temperature programed desorption (TPD), electron stimulated desorption (ESD), and X-ray photoelectron spectroscopy (XPS) to characterize both thermal and radiation induced processes in thin films formed from β-NaSn₁₃ clusters. We found that butyl group desorption occurs by both thermal and radiation induced processes, and have determined the carbon-tin bond strength and effective electron desorption cross-sections for these films. The ESD studies indicate that low energy electrons, with energies of photoelectrons, Auger electrons, and secondary electrons that would be generated during EUV exposure, can result in hemolytic dissociation of the butyl-tin bond. To improve sensitivity for the β-NaSn₁₃ clusters to radiation, we have evaluated the effect of the addition of low pressure oxygen ambient during exposure. We found that there was a significant increase in the ESD cross sections for butyl desorption. XPS experiments performed under similar low pressure oxygen ambient conditions indicate that there are significant changes in the chemical composition and chemical states of these β-NaSn₁₃ clusters during electron exposure at ultrahigh vacuum and low oxygen pressures. These studies provide a means to better understand the radiation induced processes that result in the solubility contrast of β-NaSn₁₃ clusters based photoresists, and may guide in the development of improved EUV photoresists for nanolithography.
Mechanisms in the Growth of Ultrathin Organic Films by Molecular Layer Deposition

David S. Bergsman¹*, Richard G. Closser², Mie Lillethorup³, and Stacey F. Bent¹

¹Department of Chemical Engineering, Department of Chemistry², Stanford University, Stanford, California, USA 94305. ³Department of Chemistry, Aarhus University, 8000 Aarhus, Denmark *bergsdav@stanford.edu

Molecular layer deposition (MLD) has seen increased interest in recent years for the deposition of organic thin films. This vapor-phase, layer-by-layer technique, which relies on the same self-limiting precursor saturation as atomic layer deposition, has shown promise for the development of many applications that require conformal, organic-containing coatings, such as in photoresists, lithium ion batteries, and metal organic frameworks. However, despite recent developments in MLD, there is a significant gap in our understanding of the mechanisms behind MLD and the microscopic properties of MLD-grown films, such as their nucleation behavior, their molecular-level structure, and the potential entanglement of the polymer chains. In this presentation, we will present results of our recent studies to understand such mechanisms, and discuss how that understanding can be used to better control the thermal, mechanical, and electrical properties of these materials.

To begin, we discuss our exploration of the growth behavior of organic MLD films by examining trends in film properties as a function of backbone flexibility [1]. Our results suggest that changes in growth rate between the most rigid and most flexible backbones (4 Å/cycle vs 1 Å/cycle) are not caused by differences in length of molecular precursors, chain orientation (~25° on average for each backbone), or film density (1.0 – 1.2 g/cm³), but are instead caused by an increased frequency of terminations in the more flexible chemistries. Because of the physisorption of precursors, which reintroduce reactive sites, these terminations do not lead a complete cessation of film growth. We demonstrate that this re-nucleation can even lead to growth on surfaces with a reduced number of surface sites and substrates blocked by self-assembled monolayers [2]. We further mathematically model these termination and re-initiation steps [3] and show how the model can be applied to better understand the origin of linear growth rates in MLD. We also examine the structure of the films by analyzing crystal orientation and infrared absorption data, which suggest that films consist of a mixture of upward growing chains and horizontally aligned layers of paracrystalline polymer segments.

3. M. Lillethorup, D. S. Bergsman, et al., In Revision
Toward Enhanced Oxygen Evolution Efficiency using Microstructured Nickel Surfaces

Audrey K. Taylor,1 Irene Andreu,1 and Byron D. Gates1,*

1 Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia, V5A 1S6, Canada

The renewable energy sector could benefit from the identification of regular well-defined surface morphologies that can effectively reduce the accumulation of bubbles on electrocatalytic surfaces. Specifically, the oxygen evolution reaction (OER) is an essential half reaction relevant to metal-air batteries, fuel cells, and electrolysis for power to gas applications. The morphology of surfaces of the electrodes, size and surface coverage with oxygen gas, and catalyst composition can impact the reaction efficiencies, transport of reactants and products, and fluid dynamics at the interface between the electrode and the reaction medium. Modulation of surface wettability can influence the behavior of oxygen bubbles on electrode surfaces. For instance, an increase in the hydrophilicity of the surfaces can enhance bubble release by promoting more favorable interactions with the electrolyte interface. In this work, four types of distinct regular dimpled Ni features were prepared to investigate how electrode morphology may affect the efficiency of the OER. The dimpled Ni features were created by combining the self-assembly of poly(styrene), PS, spherical templates and electrodeposition of Ni around these spherical templates. The PS templates were selectively removed by dissolution in organic solvent. The resulting geometric dimensions and roughness of the dimpled Ni features were characterized before and after electrochemical measurements by scanning electron microscopy (SEM), atomic force microscopy (AFM), water contact angle (WCA) and theoretical wetting models. The elemental surface compositions were analyzed by Auger electron spectroscopy (AES) and X-ray electron spectroscopy (XPS). Alkaline electrochemical measurements were performed to assess the efficiency of the OER using cyclic voltammetry (CV), linear sweep voltammetry (LSV), Tafel curves, and chronocoulometry (CA). The regular design of these microstructured surfaces enables a correlation of their structure with the observed function towards improving the OER.
Invited talk:

Oxidation Mechanisms of a Ni Alloy in High Temperature CO₂

Richard P. Oleksak¹, Monica Kapoor¹, John P. Baltrus², Gordon R. Holcomb¹, Ömer N. Doğan¹

National Energy Technology Laboratory, U.S. Department of Energy
¹1450 Queen Ave SW, Albany, OR 97321
²626 Cochrans Mill Rd, Pittsburgh, PA 15236

Approximately 85% of the United States’ electricity is generated via power cycles. During these cycles a working fluid (water or air) is heated to high temperatures (>500 °C) which ultimately drives a turbine to produce electricity. These cycles are built using structural alloys which have been optimized to resist significant oxidation in the harsh environments encountered during the long operating lifetimes of the power plant.

Next-generation power cycles have been proposed which utilize supercritical carbon dioxide (sCO₂) as the working fluid. If successful, these cycles may revolutionize the power generation industry by offering significantly improved conversion efficiencies as well as other economic and environmental benefits relative to current power cycles. One of the primary barriers to the implementation of this technology is the unknown compatibility of structural alloys in high temperature CO₂-rich environments. The Structural Materials Team at NETL is working to solve this issue by evaluating the oxidation/corrosion behavior of a variety of alloys in environments relevant to sCO₂ power cycles.

In this presentation, we show results of a candidate Ni alloy exposed to high temperature CO₂ for times ranging from 5 minutes to 500 hours. The resulting surface oxides were characterized in detail using TEM, XPS, and atom probe tomography, with an emphasis on understanding the effects of early stage phenomena on the long-term oxidation resistance of the alloy. In addition to assessing the suitability of this class of Ni alloys for sCO₂ power cycles, the results shed light on early-stage processes which likely play an important role in the oxidation behavior of many structural alloys.
Supercritical Carbon Dioxide (sCO₂) has been identified as a candidate fluid for advanced power cycles. The sCO₂ Brayton cycle is considered for a wide variety of power conversion systems such as: nuclear, geothermal, coal, natural gas, and any system that converts heat energy into electrical energy. The need for corrosion data on energy systems materials is a primary concern for developing more efficient power production facilities. This project examines the ability to collect stress corrosion cracking and low frequency fatigue data in environments that energy system materials would experience. The elevated temperatures (500-800 °C) and high pressures (up to 25 MPa) of these cycles make it challenging to use traditional test methods; therefore, the tests are being performed using new equipment recently developed at Idaho National Laboratory. The corrosion resistance of unstressed materials, tested at these temperatures and pressures, will be displayed as well as calibration and set up of the cracking data collection device.
Reactive molecular dynamics modeling of classical models of iron/electrolyte interface

Hossein DorMohammadi\textsuperscript{1}, Qin Pang\textsuperscript{3}, Liney Arnadottir\textsuperscript{3}, O. Burkan Isgor\textsuperscript{1}
\textsuperscript{1} Oregon State University, School of Civil and Construction Engineering, Corvallis, Oregon, USA
\textsuperscript{2} Oregon State University, School of Chemical, Biological and Environmental Engineering, Corvallis, Oregon, USA

Abstract: Three known classical models of the Electrical Double Layer (EDL), e.g. Helmholtz, Gouy-Chapman and Stern models are applied to investigate the iron/electrolyte interface reactions. Passivity of iron in highly alkaline environment using Reactive Force Field Molecular Dynamics (ReaxFF-MD) is investigated. Simulations were performed on Fe(110) surface and the electrolyte contains NaOH to simulate highly alkaline environment as we have in concrete with pH=13.5. The passivation of iron was observed with Stern model. The simulation results are in good agreement with experimental results and supports the expected thermodynamic behavior. The passivation pattern involved dissociation of NaOH to charged Na and OH, dissociation of water into charged OH, H$_3$O, O, and H species, formation of a charged layer of iron atoms at the iron-solution interface, and the diffusion of oxygen into iron to form iron oxides. A control study to investigate the capability of Stern model for simulating metal/electrolyte interface was performed. Iron corrosion in contact to electrolyte with pH=7 containing NaCl was observed as it is expected thermodynamically.

Keywords: Iron passivity; Molecular Dynamics (MD), Reactive Force Field (ReaxFF); Stern model.
Effects of Surface Defects on the Interactions of Cl and α-Fe₂O₃ (0001)
Surface: A Density Functional Theory Study

Qin Pang⁹, Hossein DorMohammadi¹, O. Burkan Isgor¹, Líney Árnadóttir⁹

⁹School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, OR, 97331, United States
¹School of Civil and Construction Engineering, Oregon State University, Corvallis, OR, 97331, United States

Fe (III) oxides are considered by many to be the dominant structure of the outer layer of the iron passive film formed in alkaline electrolytes. Some aggressive ions, such as chloride, can induce depassivation of these passive films. Here hematite (α-Fe₂O₃) is used to represent the Fe (III) oxides to study the mechanism of depassivation of the iron passive film. The interactions of Cl with both pristine α-Fe₂O₃ (0001) surface and surfaces with different defects are studied. Total of four surfaces are considered: pristine surface, Fe vacancy surface, O vacancy surface and Fe-O pair vacancy surface. We found that the surface defects affect the adsorption strength of Cl on the surface. The adsorption of Cl is strongest on O vacancy surface, followed by the adsorption on Fe-O pair vacancy surface, pristine surface and Fe vacancy surface. The stability of the Cl in the sub surface was studied on the four surfaces and was found to be unfavorable relative to the surface adsorption. The reaction energy for Cl going to the sub surface is less unfavorable on the O vacancy surface and Fe-O pair vacancy surface than on the other two surfaces. The Cl insertion process through an O vacancy has insertion reaction energy of around 0.5 eV, which is about 1 eV lower than that on the pristine surface. The coverage of Cl can influence the insertion reaction energy and higher coverage of Cl can make the reaction less unfavorable.
Ultra-high-vacuum scanning tunneling microscopy and spectroscopy are used to spatially resolve the topography and electronic band modifications of graphene by atomic oxygen in the nanometer scale. We show that oxygen radicals, even at a low surface coverage of O/C = ~1/150, form random surface distributions and clusters of various sizes. These oxygen adsorbates are also observed to be $p$-type dopants, which leads to site-dependent partial and full band modifications up to a gap of few hundred meV. The degree of band gap opening and the number of O-atom induced charge-holes per area are inversely proportional to the distance to the nearest adsorbate. However, the number of holes contributed per oxygen atom was found to be a site-independent constant of 0.15±0.05. For a small population of adsorbates taller than 4Å, the graphene energy bands are no longer resolved; instead STS measurements show very spatially localized but high density of states over a wide energy range, which indicates sole tunneling contribution from the cluster of electron-rich O-atoms and a complete decoupling from the graphene bands.

References:
Formation of Metastable Water Chains on Anatase TiO$_2$(101)

Arjun Dahal and Zdenek Dohnálek

Physical and Computational Sciences Directorate and Institute for Integrated Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, United States.

The interaction of water with metal oxide surfaces is of great importance in many diverse areas such as catalysis, electrochemistry, corrosion, atmospheric science, geology, astrophysics, and others. Anatase TiO$_2$ surface is particularly relevant because it is the most active polymorph of TiO$_2$ and its commercially employed nanomaterials grow preferentially as anatase. In this study, we employ scanning tunneling microscopy (STM) to study the adsorption of water on a model stoichiometric anatase TiO$_2$(101) surface. Well-defined anatase TiO$_2$(101) surface has saw-tooth-like morphology exposing alternating rows of two-fold-coordinated oxygen atoms (O$_{2c}$) and five-fold-coordinated Ti atoms (Ti$_{5c}$) along the [010] direction. Our STM data show that at 80 K isolated water monomers bind molecularly to the Ti$_{5c}$ sites. The onset of diffusion is found at ~190 K where water monomers diffuse both along and across the Ti$_{5c}$ rows. The analysis shows that the along-the-row diffusion is energetically favored by only 0.03 eV. Surprisingly, we find that at 80 K water molecules start to form linear chains along the Ti$_{5c}$ rows as the coverage is increased. This indicates the presence of transient mobility of water molecules suggesting that the adsorption occurs via a precursor state. When the water chains are annealed at 190 K, they fall apart to monomers that reside on the next-nearest-neighbor Ti$_{5c}$ sites. These results demonstrate that the water chains are metastable in nature. This is at odds with many other oxide surfaces where hydrogen-bonded water clusters are energetically preferred over the isolated monomers.

Key words: Adsorption, monomers, diffusion, linear chains, mobility
In situ Molecular Verification of Ethanol Electrocatalysis Mechanism at Polycrystalline Gold Electrode Surfaces

Yanyan Zhang,a,b,c* Jungang Wang,a Zihua Zhua

a Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354 (USA).
b Beijing National Laboratory for Molecular Sciences, National Centre for Mass Spectrometry in Beijing, CAS Key Laboratory of Analytical Chemistry for Living Biosystems, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190 (China).
c University of Chinese Academy of Sciences, Beijing 100049, China.
E-mail: yanyan.zhang@pnnl.gov

Abstract:
Electrocatalysis, a heterogeneous catalysis reaction that happens at the surface or within a few monolayers of the surface of catalyst, has significant applications such as organic electrosynthesis, electrode sensors, electrolysis, and especially in the case of fuel cells. The fundamental understanding of the overall electrocatalytic process will be greatly beneficial to the designing of novel catalysts with high efficiency. Extensive studies have been carried out to characterize the morphological and chemical state changes of the electrode surface during electrocatalysis processes. However, direct molecular evidence of the relationship between the chemical state of the electrode surface and its electrocatalytic activity is still lacking. Here, we used an innovative in situ liquid SIMS approach to investigate the molecular structure of a gold electrode surface and its link to the electrooxidation efficiency of ethanol in a KOH aqueous solution. We started SIMS measurement when a negative potential was applied to the electrode under which electrooxidation of ethanol could not occur, increased the potential step-by-step until a thick Au oxidation layer grew on the Au electrode surface, and then gradually decreased the potential back to the original value. Au(OH)n− ions were observed to increase with potential increasing at the very beginning, indicating formation of Au-OH at the Au electrode surface. At the same time, the oxidation product, CH3CO2− increased, too, suggesting that electrocatalysis occurred. However, when potential became more positive, Au(OH)n− and CH3CO2− signal intensity decreased, in well agreement with formation of an Au oxide layer under high potential, and decreasing of electrocatalysis efficiency. When the potential decreased, Au(OH)n− and CH3CO2− signal intensities increased again, suggesting that Au-OH structure came back and electrocatalysis activity recovered. However, when the potential decreased to the original value, Au(OH)n− and CH3CO2− signal intensities decreased again, suggesting the disappearance of Au-OH structure as well as the electrocatalysis activity of the electrode. Our work gives direct molecular evidence about the relationship between the Au-OH structure and the electrooxidation efficiency of ethanol on gold electrode surface, which has not been reported before. This work also demonstrated the unique capability of the in situ liquid SIMS approach in molecular probing complex chemistry occurring at various solid/liquid interfaces.
G1: Probing anion and molecular specificities using electrospray ionization photoelectron spectroscopy

Qin-qin Yuan, 1,2 Zheng Yang,1 Gao-Lei Hou,1 and Xue-Bin Wang*, 1

1 Physical Sciences Division, Pacific Northwest National Laboratory, P. O. Box 999, MS K8-88, Richland, Washington 99352, USA
2 Dalian Institute of Chemical Physics, Chinese Academy of Sciences 457 Zhongshan Road, Dalian, Liaoning 116023, China

Ion specificity, a widely observed macroscopic phenomenon in condensed phases and at interfaces, is a fundamental chemical physics issue. Herein we report our recent studies of such effects using cluster models in an “atom-by-atom” and “molecule-by-molecule” fashion not possible with the condensed-phase methods. We use electrospray ionization (ESI) to generate molecular and ionic clusters to simulate key molecular entities involved in local binding regions and characterize them by employing negative ion photoelectron spectroscopy (NIPES). In this poster, we present three recent studies using ESI-NIPES. (1) We studied the structures, energetics, and optical properties of hydrated clusters of the cis-pinonate anion (cPA\(^{-}\)), the deprotonated form of cis-pinonic acid. Our results show that cPA\(^{-}\) can adopt two different structural configurations – open and folded. In the absence of waters, the open configuration has the lowest energy and provides the best agreement with the experiment. The added waters, which mainly interact with the negatively charged –CO\(_2\)- group, gradually stabilize the folded configuration and lower its energy difference relative to the most stable open-configured structure. Thermochemical and equilibrium hydrate distribution analyses suggest that the mono- and di-hydrates are likely to exist in humid atmospheric environments with high populations. (2) Recently, we observed that at high temperatures, NIPE signal exhibits a depletion of the intensity compared to that at the low temperature for the (HCOO\(^{-}\))(H\(_2\)SO\(_4\)) anion pair. Formation of (HCOO\(^{-}\))(H\(_2\)SO\(_4\)) clearly violates the gas-phase acidity predictions. Accompanying theoretical studies confirm the existence of (HCOO\(^{-}\))(H\(_2\)SO\(_4\)) pair, which is slightly lower in energy than the conventional (HCOOH)(HSO\(_4\)\(^{-}\)) structure by formation two strong hydrogen bonds. Ab initio MD simulations unravels that despite (HCOOH)(HSO\(_4\)\(^{-}\)) being favored by energy, it suffers strong entropic penalty, and readily converts to its conventional form of (HCOOH)(HSO\(_4\)\(^{-}\)) by increasing temperature. (3) Three newly synthesized [Na\(^{+}\)(221-Kryptofix)] salts containing AsCO\(^{-}\), PCO\(^{-}\), and PCS\(^{-}\) anions were successfully electrosprayed into a vacuum, and these three ECX\(^{-}\) anions with linear geometries were investigated by NIPES and high-resolution photoelectron imaging spectroscopy. The electron affinities (EAs) and spin-orbit (SO) splittings of ECX\(^{-}\) were determined from the spectra to be AsCO\(^{-}\): EA = 2.414 ± 0.002 eV, SO splitting = 988 cm\(^{-1}\); PCO\(^{-}\): EA = 2.670 ± 0.005 eV, SO splitting = 175 cm\(^{-1}\); PCS\(^{-}\): EA = 2.850 ± 0.005 eV, SO splitting = 300 cm\(^{-1}\). PCS\(^{-}\) has the greatest EA of the three triatomic molecules considered here that is counterintuitive based upon simple electronegativity considerations. This finding is understandable in terms of the movement of electron density from phosphorus in the HOMO of PCO\(^{-}\) to sulfur in the HOMO of PCS\(^{-}\).
G2: An Overview of In situ Liquid Secondary Ion Mass Spectrometry

Xiaofei Yu1,3, Xiao-Ying Yu2, Zihua Zhu1

(1) W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354 USA;
(2) Earth and Biological Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA
(3) School of Physics, State Key Laboratory of Crystal Materials and Key laboratory of Particle Physics and Particle Irradiation (MOE), Shandong University, Jinan, P. R. China, 250100

Xiaofei.Yu@pnnl.gov

Abstract: Time-of-flight secondary ion mass spectrometry (SIMS) is a powerful surface analysis tool which can provide elemental, isotopic and molecular information with a nanoscale spatial resolution. However, SIMS is a high vacuum technique; therefore traditionally only solid samples can be analyzed. In situ liquid SIMS, which enabled by System for Analysis at the Liquid Vacuum Interface (SALVI), was developed in Pacific Northwest National Laboratory (PNNL) in last several years, allowing in situ analysis of various liquids and liquid interfaces. In brief, a liquid sample is sealed in a vacuum compatible microfluidic liquid cell (i.e., SALVI), below a thin (e.g., 100 nm) SiN membrane. During measurement, a primary ion beam is focused with a submicrometer size, drills an aperture through the SiN membrane, and through the aperture the liquid (and liquid interface) can be analyzed. If the diameter of the aperture is smaller than 3 microns, the surface tension of an aqueous liquid can hold the liquid without any spraying out. At the same time, the liquid evaporation from such a small aperture is not a problem for SIMS measurement. In situ liquid SIMS can provide molecular information from many liquids and liquid interfaces that could not be obtained by any other techniques. In this presentation, the principle and several successful applications of in situ liquid SIMS will be introduced.

G3: Optically Transparent Glass from Microfluidic-assisted Sol-Gel 3D-Print

Yujuan He, Alvin Chang, Chih-Hung Chang

The three-dimensional (3D) printing technology has quickly aroused the enthusiasm of the research in the fields of manufacturing and medical treatment. With different printing mechanisms, the computer-designed products such as small clips, an Urbee car and a biodegradable human bone scaffold 1 were successfully printed without any mold. To serve the various needs, polyamide, resin, metals and ceramics were commonly applied as the 3D-printing materials. However, printing the transparent glass is still a technical challenge. Although the binder approaches which glued the glass powders into bulk can overcome the high melting temperature, their final products were very fragile and opaque because of the scattering. In 2015, the group of Neri Oxman in MIT 2 reported the 3D-print of transparent glass objects by a fused deposition method at glass melting temperatures. Their repeatable procedure of printing the light transmitted and mechanically firm glass-objects is an important breakthrough of 3D-printing. However, three main drawbacks of this procedure constraints its further applications: 1) to maintain the high temperature (~ 1000°C) to keep the liquid glass requires expensive and complicated constructions and handlings of the print head; 2) the gravity-driven flow rate is hard to control since it depends on many varieties; 3) the printed parts has a minimum radius of 22 mm and a draft angle of 28°. Herein, we introduce the microfluidic-assisted sol-gel print head to generate the glass “ink” for 3D-printing. The pH of an acid stream of aluminum-silica precursors were increased by mixing with a base stream containing either NaOH or NH₄OH. Combining this pH modification with the control of the residence time in the micro-tube and precursor concentrations, the condensation and polycondensation of silica sol-gels were efficiently accomplished. Two oil side-streams were applied after the mixing point to smoothly deliver the silica gels in the tube during their formation. Finally, the outcome silica gel was placed onto a stage/container in different temperatures. The stage temperature which hardens the soft silica gel into the xerogel will be investigated in this research. The printed products were cured by slowly raising the temperature from 60°C to 800°C. This easily accessible set-up and energy-saving procedure will enable more possibilities of the 3D-printed transparent glass. The smaller dimensions compare to Neri’s procedure is also reachable by simply changing the diameter of the micro-tubes.

Reference

G4: Coming Together Under Pressure: Using Surface Analytical Tools to Dissect the Role of Fibril Formation in the Frog Sticky-Tongue Mechanism

J Elliott Fowler1, Thomas Kleinteich2, Johannes Franz3, Daniel A. Fischer4, Tobias Weidner3,5, Stanislav Gorb2, Joe E. Baio1

1Oregon State University, Chemical, Biological and Environmental Engineering Department, Corvallis, OR; 2Zoological Institute of the University of Kiel, Department of Functional Morphology and Biomechanics, Kiel, Germany; 3Max Planck Institute for Polymer Research, Mainz, Germany; 4National Institute of Standards and Technology, Gaithersburg, MD, USA; 5Department of Chemistry, Aarhus University, Aarhus, Denmark

In the blink of an eye, frogs capture their prey with a highly-specialized tongue. Recent studies indicate this tongue is covered with finger-like papillae and a shear-thinning mucus that acts as a pressure sensitive adhesive. The mucus undergoes a chemical change and becomes sticky in response to strain. However, no chemical analysis of frog tongue mucus has been performed to validate this mechanism. Thus, the goal of this experiment is to examine the chemical structure of the mucus following capture of prey with complimentary surface analytical tools. Previous studies of mucus from other animals suggests that mucus from a frog’s tongue likely consists of mucins - serine, threonine and proline (STP) rich glycoproteins conjugated in a bottle-brush formation with O- and N-linked oligosaccharides. Therefore, we expect to see chemical bonds associated with glycoproteins, as well as evidence of fibril formation at the mucus-tongue interface. To test this hypothesis, we collected both near-edge x-ray absorption fine structure (NEXAFS) microscopy images and sum frequency generation (SFG) vibrational spectra from layers of mucus left after frog tongue strikes on cleaned glass slides. NEXAFS imaging demonstrates a uniform distribution of amide, hydroxyl and carbon-carbon bonds across the mucus surface at 402 eV, 288 eV and 298 eV, respectively. Difference spectra (70°-30°) of individual N1s and C1s K-edge spectra pulled from these images indicate a large positive dichroism for amide π* bonds, a small positive dichroism for hydroxyl σ* bonds and no dichroism for carbon-carbon σ* bonds, consistent with fibril formation and disorder of oligosaccharide groups near the mucus surface. SFG spectra in the C-H stretching region reveal features near 2858 cm⁻¹, 2878 cm⁻¹ and 2931 cm⁻¹ assigned to CH₃,sym, CH₂,sym and CH₃,fermi modes, respectively. These modes likely stem from serine and threonine within the mucin protein. Combined, this work suggests that glycoproteins are well-ordered at the mucus-air interface.
G5: Particles in Organic Boxes: Scanning Tunneling Spectroscopy of Molecular Electronic Structure

B.N. Taber and G.V. Nazin
Department of Chemistry and Biochemistry, University of Oregon, 1253 University of Oregon, Eugene, OR, 97403, USA

The particle-in-a-box (PIAB) model is a commonly used teaching tool in introductory quantum mechanics courses, describing a particle that is confined within an infinite potential well. Classically, the particle can travel at any speed within the box and can be found at any position. As the box becomes small, however, quantum effects dominate and the particle can only have discrete non-zero energies, and may only be detected in certain positions. Here, we present real-space scanning tunneling microscopy/spectroscopy (STM/STS) measurements of organic molecules adsorbed on noble metal (111) surfaces that exhibit one- and two-dimensional PIAB-like behavior. First, we examined the electronic structure of different alkyl-substituted oligothiophenes [Phys. Chem. Chem. Phys., 18, 4842-4849 (2016); J. Chem. Phys. 144, 194703 (2016)]. STM imaging showed that on Au(111), oligothiophenes adopted distinct straight and bent conformations. By combining STS maps with STM images, we visualized, in real space, particle-in-a-box-like oligothiophene molecular orbitals. These results demonstrate that different planar conformers with significant geometrical distortions of oligothiophene backbones surprisingly exhibit very similar electronic structures, indicating a low degree of conformation-induced electronic disorder, and consequently lower probability of charge carrier trapping within molecular backbones in poly- and oligothiophene materials. Second, we studied the electron confinement within individual ring-shaped cycloparaphenylene (CPP) molecules forming self-assembled films on Ag(111) and Au(111) surfaces [J. Phys. Chem. Lett., 7, 3073–3077 (2016)]. We used a particle-in-an-elliptical-box (PIAEB) model to describe the confined surface states, finding a correlation between molecular eccentricity and confined surface state energy, suggesting a route for controllable and scalable modification of surface electronic structure. Combined, these studies demonstrate that the PIAB model for electronic structure transcends the confines of introductory quantum textbooks.
Indium gallium zinc oxide (IGZO) thin-film transistors (TFT) are revolutionizing the display industry where both higher resolution and higher refresh rates are enabled compared to amorphous silicon TFTs. Recent studies have indicated that field effect sensors (FES) can also be made using IGZO where a wide range of biomarkers can be detected. Selectivity for these biosensors is obtained through immobilization of enzymes on the IGZO-FES back-channel surface by cross linking with aminosilane surface groups. Integrating fully transparent IGZO-FES onto transparent, flexible substrates may enable smart contact lens which can sense biomarkers in tear fluid, with a primary focus to measure glucose concentrations for individuals with Type 1 diabetes. We have recently demonstrated the use of fully transparent, field-effect sensors to continuously monitor glucose concentrations down to 10 µM. The current study focuses on evaluating the physical and electrical stability of IGZO-FESs under conditions that simulate human tears. The dissolution kinetics were monitored using ellipsometry, changes in surface roughness were characterized using atomic force microscopy, preferential etching was determined using X-ray photoelectron spectroscopy, and electrical performance was characterized by measuring transfer curves. We find that the aminosilane layer significantly stabilizes the surface chemistry, and that IGZO-FESs should be amenable for a wide range of biomedical sensing applications.
G7: Ambient pressure X-ray photoelectron spectroscopy investigation of radiation induced chemistries of organotin clusters

J. Trey Diulus¹, Ryan T. Frederick¹, Mengjun Li², Danielle Hutchison³, Morgan R. Olsen³, Igor Lyubinetsky¹, Liney Árnadóttir¹, Eric L. Garfunkel², May Nyman³, Hirohito Ogasawara⁴, Gregory S. Herman¹,3*

¹School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR, 97331, USA
²Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, USA
³Department of Chemistry, Oregon State University, Corvallis, OR, 97331, USA
⁴SLAC National Accelerator Laboratory, Menlo Park, CA 94025 USA.

Organometallic chemistries provide unique control over the size, shape, and structure of nanoscale clusters. Applications for these clusters can range from supported catalysts to biomedical imaging agents to precursors for nanoscale materials. Radiation induced processes allow the removal of ligands from these clusters at low temperatures, which allows the retention of the internal coordination of the cluster and minimizes agglomeration or other structural transformations. In this study, we are investigating the interaction of soft X-ray radiation with organotin based clusters to better understand the transition from organometallic to metal oxide clusters. As a model system we are studying the sodium templated butyl-tin Keggin (β-NaSn₁₃) cluster [NaO₄(BuSn)₁₂(OH)₃(O)ₙ(OCH₃)₁₂(Sn(H₂O)₂)]. These clusters were spin-coated to form thin films (~20 nm thick), which were then characterized using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). Experiments were performed for photon energies above and below key absorption edges, and for oxygen, nitrogen, and hydrogen partial pressures between 0.01 to 1 Torr. AP-XPS was used to monitor changes in relative concentrations and chemical states using the Sn 3d, O 1s, and C 1s core-levels. A significant reduction in the C 1s signal versus exposure time was observed, where the oxygen partial pressure was able to modify the rate of butyl group desorption from the β-NaSn₁₃ clusters. These studies enhance the understanding of radiation induced processes in β-NaSn₁₃ based thin films and provide mechanistic insights for the formation of tin oxide nanomaterials at surfaces.
Interfaces of metal/metal oxides are essential in many scientific and technological applications due to their impact on the composite structure and properties of materials. For example, metal oxides are used as thermal barriers to shield metals in high temperature environments like steam turbines. Metal/oxide interfaces also occur in metal medical implants, in electronics devices, and in heterogeneous catalysts. γ-Al2O3 is a polymorph of Al2O3 commonly used as a catalyst support because its high surface area makes it suitable for the efficient dispersal of metal catalysts, such as Pt, Pd, Ru, and Rh. The atomic structure and chemical interactions at the interface of these materials can significantly impact the electronic and mechanical properties of the catalyst and the support. This work combines theoretical and experimental methods to study the nature of the metal/metal oxide interface between γ-Al2O3 and Pt. In the theoretical approach, density functional theory (DFT) was used to study the surface atomic structure and then interactions of the oxide with Pt(111) at the interface. To predict the effect of the environment on the stability of the surface planes, the surface energy of three different low index planes of γ-Al2O3 and their possible terminations were calculated as a function of partial pressures of oxygen at the experimental fabrication temperature (1100K). The (100) surface plane of γ-Al2O3 was found to be most stable and the (111) surface plane had the highest surface energy (corresponding to lowest stability) due to its highly polar structure. The stoichiometric terminations were found to be the most stable for the (100) and (110) planes at all partial pressures of oxygen, while the most stable termination of the (111) plane transitions from the stoichiometric surface to an oxygen rich surface termination with oxygen higher partial pressure. On this basis, separate sandwich structure models of Pt(111) and three surface terminations of γ-Al2O3 (111) were made and their interfacial energies were calculated. At the relatively low temperature of 600K, the Pt(111) interacting with oxygen terminated alumina had the lowest interfacial energies at all oxygen partial pressures due to relatively strong ionic Pt-O bonds at the interface. The next lowest interfacial energy was for the Pt(111) on stoichiometric Al-terminated alumina due to weaker metallic Pt-Al bonding at the interface, which is also independent of the oxygen partial pressure due to its surface charge neutrality prior to interaction with Pt atoms. The model of Pt(111) on a non-stoichiometric Al2-terminated interface resulted in the highest interfacial energy and is, hence, the most unstable. Interfacial energies in each case were observed to increase with in temperature from 600K through 800K, 1000K to 1200K. This provides the basis for the experimental study of the atomic structure of the interface between γ-Al2O3 and Pt nanoparticles.
Abstract

Infrared (IR) gas sensing technique is commonly used for carbon dioxide (CO₂) sensing due to its high sensitivity, selectivity and stability. However, the IR apparatus are usually expensive and difficult to be miniaturized. Therefore there is a need to investigate new approaches of low-cost IR sensing. Copper sulfide (CuₓS), a non-toxic, low-cost and earth-abundant material, exhibits localized surface plasmon resonance (LSPR) throughout the near- and middle-IR region and can be used as LSPR-based sensing material. In this work, CuₓS thin films were facially synthesized by a modified successive ionic layer adsorption and reaction at room temperature, followed by a low-temperature annealing treatment in air. The annealed CuₓS thin films possessed a nanostructure consisting of CuₓS nanoflakes and exhibited suitable optical property for IR gas sensing. The resulting CuₓS-based thin film sensor demonstrated a low detection limit of 100 ppm for CO₂.
G10: Density Functional Theory Study of CO2 dissociation of Ni(111) surface

Weinan Zhao, Líney Árnadóttir

1School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR, 97331, USA

Abstract
The corrosion and degradation of Ni and its alloys in supercritical carbon dioxide (S-CO2) is a merging issue for material selection for implementation of S-CO2 thermal cycles in industry. The initial steps of corrosion and degradation are here considered to be the surface oxidation and carburization upon CO2 dissociation. In this study, we applied Density Functional Theory (DFT) to study the initial steps of carburization of Ni (111) surface in CO2 environment. The overall carburization reaction, CO2 ↔ Cads + O2 can be broken into four elementary steps, CO2 adsorption, two surface reactions, CO2 dissociation to CO and O followed by dissociation on CO to O and C, the last step is O2 desorption. In this initial study we concentrate on the thermodynamics of the two surface reactions and determine their activation barriers. We determine the most stable adsorption sites for CO2 and its dissociated products to compare the thermodynamics of the different elementary reactions steps. On Ni (111), CO2 is most stable at a hollow site but the interactions are very weak with adsorption energy 0.24 eV which is 0.12 eV lower than reference. The coadsorption of CO and O, which are products of the first step of CO2 dissociation, are most stable on fcc site and hcp site respectively. And the interactions between the two adsorbates are slightly repulsive. This initial CO2 dissociation step is slightly exothermic, 0.33 eV, but the kinetic barrier is rather high, 0.86 eV. The further dissociation of CO to C and O is endothermic by more than 2 eV and has large activation barrier, 3.4 eV, while the reverse reaction, combination of C and O to form CO is endothermic and has a barrier of 1.2 eV. The results of CO dissociation are in good agreement with previous literature. The high barriers makes this reaction path unlikely to be the main reaction path for the carburization of Ni surface but co-adsorbates and surface defects are likely to play a major role in this process.
G11: In Situ Observation of Catalyst Reconstruction During Electrochemical CO2 Reduction

Maoyu Wang,1 Zhe Weng,2 Yuesheng Wu,2 Hailiang Wang,2 Zhenxing Feng,1,*

1School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, Oregon, 97331, United States
2Department of Chemistry, Yale University, New Haven, Connecticut, 06520, United States
*E-mail: zhenxing.feng@oregonstate.edu

Abstract
Overconsumption of fossil energy has increased the CO2 concentration in the atmosphere, leading to severe climatic problems. Toward establishing a sustainable energy system, it is desirable to develop carbon-neutral fuels, for which a promising approach is electrochemical conversion of CO2 to useful products powered by electricity generated from renewable energy sources. However, due to slow kinetics and diverging reaction of electrochemical CO2 reduction, high-performance catalysts are required. In this work, we have designed three copper (Cu)-complexes and one of them (CuPc) have exhibited high efficiency and selectivity for electrochemical reduction of CO2 to methane. Using in situ X-ray absorption spectroscopy we find CuPc undergoes reversible structural and oxidation state changes to form nanometer size Cu metallic clusters, while the other two decompose irreversibly. With the help from density functional theory, the small but stable Cu clusters generated in situ during reaction is identified as the reaction active site of electrochemical CO2 reduction and is responsible for CuPc’s high efficiency and selectivity. The insights learned from this study provide new ways to control the catalytic site at molecule level for the development of high electrocatalytic nano-materials.
G12: Scalable fabrication of patterned ZnO nanostructures by using microreactor-assisted nanoparticle deposition process and microfluidic channels

Zhongwei Gao, Peilun Zhang, Chih-hung Chang
Chemical engineering school, Oregon State University, Corvallis, OR 97330

In this study, we developed a method to fabricate a patterned films by using a combination of microreactor-assisted nanoparticle deposition (MAND) process and microfluidic channels. The MAND process is capable of generating nanoscale building blocks with controlled sizes, ranging from molecule clusters to nanoparticles, which allows for a more controlled and precise growth of nanostructures. Those nanomaterials serve as building blocks that can be delivered to the substrate surface through the microfluidic channels for a patterned film growth. The microfluidic channels are made of cured polydimethylsiloxane (PDMS) by using a replication from a patterned SU-8 photoresist-coated glass. By combining the two process together, ZnO nanorods were successfully deposited on glass substrate. The mass transfer and the deposition mechanisms and kinetics were also studied. The scaling up for the MAND was achieved by numbering-up the microchannel unit operations in parallel, allowing for the deposition of the films on various scales.
G:13 Long silver nanowire synthesis and its application

Han Mei, Chih-hung Chang

School of Chemical, Biological, and Environmental Engineering, Oregon State University

Abstract:

Transparent conducting films (TCFs) are a critical component in many personal electronic devices. Transparent and conductive doped metal oxides are widely used in industry due to their excellent optoelectronic properties as well as the mature understanding of their production and handling. However, they are not compatible with future flexible electronics developments where large-scale production will likely involve roll-to-roll manufacturing. Recent decade, researchers were attempting to develop metal nanowires and other conductive material for example: carbon nanotubes, graphene thin films. Silver nano-wires drew tremendously attention, due to its great heat and electronic properties, high aspect ratio nanowires are showing very good performance like: low square resistance, nearly 85% transparency and relatively low cost in manufacturing process. Once these lab stayed results can be applied in industry, it will be a milestone to make life cheaper and easier.
G14: Determination of Amorphous Precursors Under Various Deposition Pressures and Their Effects on the Crystalline Phase Distribution of TiO$_2$ Thin Films Deposited by Pulsed Laser Deposition

1Okan Agirseven, 1James E.S. Haggerty, 1Janet Tate, 2Laura T. Schelhas, 2Kevin H. Stone, 2Michael F. Toney, 3Lauren Garten, 5John Perkins, 3David S. Ginley, 4Vladan Stevanovic, 4Brian P Gorman, 5Kirill Popov, 5Daniil Kitchaev, 5Wenhao Sun, 5Gerbrand Ceder

1Oregon State University, Corvallis, OR
2Stanford Synchrotron Light Source, Menlo Park, CA
3National Renewable Energy Laboratory, Golden, CO
4Colorado School of Mines, Golden, CO
5Lawrence Berkeley National Laboratory, Berkeley, CA

ABSTRACT
TiO$_2$ is a versatile wide bandgap transparent semiconducting oxide with four well known polymorphs, anatase, rutile, brookite and TiO$_2$ (B). The crystalline polymorphs of TiO$_2$ require high temperature annealing processes to form from an amorphous precursor. These crystal structures are desired for many industrial applications mainly for their photocatalytic activity. However, in the current literature, the correlations of precursors with the end products are still unclear. Our research aims to understand the formation behaviour of these metastable polymorphs of TiO$_2$ as related to precursor properties such as defects and density. In this study, TiO$_2$ thin films deposited at room temperature on fused silica substrates by pulsed laser deposition under different oxygen pressures. All the films were annealed with same annealing process. However, changing the oxygen pressure during the deposition resulted in different phase structures and phase fractions after the annealing processes. We found that the precursors deposited at the lower pressure form rutile, and at higher pressures form anatase only. Microstructural properties of TiO$_2$ thin films are investigated by XRD, Raman spectroscopy, SEM, XPS, and optical transmission and reflection spectroscopy.
C1: Structures, Energetics and Interactions of Aerosol Related Species and Clusters

Zheng Yang,1 Zhengbo Qin,1,2 Gao-Lei Hou,1 Marat Valiev,3 and Xue-Bin Wang1

1Physical Sciences Division, Pacific Northwest National Laboratory, P. O. Box 999, MS K8-88, Richland, Washington 99352, USA
2Institute of Atomic and Molecular Physics, Anhui Normal University, Wuhu, Anhui 241000, China
3Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, Richland, Washington 99352, United States

Inorganic and organic clusters related to aerosol formation were studied using negative ion photoelectron spectroscopy (NIPES) and theoretical modeling. For inorganic clusters, three short-lived, anionic intermediates, ISO3–, IS2O3–, and IS2O4–, are detected during reactions between ozone and aqueous iodine/sulfur oxides microdroplets. The NIPE spectra reveal that all of the three anionic species are characterized by high adiabatic detachment energies (ADEs) – 4.62 ± 0.10, 4.52 ± 0.10, and 4.60 ± 0.10 eV for ISO3–, IS2O3–, and IS2O4–, respectively. High level CCSD(T) calculations reveal that the lowest energy structures are characterized by formation of I–S and S–S bonds and can be structurally viewed as SO3 linked with I, IS, and ISO for ISO3–, IS2O3–, and IS2O4–, respectively. The obtained intrinsic molecular properties of these anionic intermediates and neutral radicals should be useful to help understand their photochemical reactions and chemical transformation in the atmosphere. As for the organic species, homogeneous dicarboxylic acid complexes: (HO2(CH2)nCO2–[HO2(CH2)nCO2H], n = 0-12) were investigated. The results imply that dicarboxylic acids not only can contribute to the heterogeneous complexes formation involving sulfuric acid and dicarboxylic acids but also can promote the formation of homogeneous complexes by involving dicarboxylic acids themselves. Cis-Pinate–H2O/CH3CN/CH3OH Complexes were also studied. We discovered that Cis-pinate dianion prefers to be solvated alternately on the two –CO2– groups with increase of solvent coverage; the asymmetric type isomers for cis-pinate–(H2O)2 and cis-pinate–(CH3OH)2 exist; and formation of inter-solvent H-bonds between H2O and CH3CN is favorable in mixed solvent clusters, but not between H2O and CH3OH.
C2: In situ Characterization of Switchable Ionic Liquids by Liquid ToF-SIMS and SALVI

Juan Yao, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354
David B. Lao, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354
Xiao Sui, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354
Yufan Zhou, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354
Satish K. Nune, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354
Zihua Zhu; Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354
David Heldebrant, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354
Xiao-Ying Yu;* Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354

Abstract:
Switchable ionic liquids (SWILs) derived from organic bases and alcohols are attractive due to their applications in gas capture, separations, and nanomaterial synthesis. However, their exact solvent structure still remains a mystery. We present the first chemical mapping results of the solvent structure of two SWILs using in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS). The first system consists of two components including 1,8-diazabicycloundecene (DBU) and 1-hexanol and the second system has a single component of 1-((1,3-dimethylimidazolidin-2-ylidene)amin)propan-2-ol (kochanol) as both the acid and base. SWIL chemical speciation is found to be more complex than the known stoichiometry. Dimers and ionic clusters have been identified in SIMS spectra; and confirmed to be the chemical species differentiating from non-ionic liquids via spectral principal component analysis. In situ chemical mapping discovers two coexisting liquid phases and a molecular structure vastly different from conventional ionic liquids when the SWIL is loaded with an acidic gas like carbon dioxide (CO2). Our unique in situ molecular imaging has advanced the understanding of SWIL chemistry and how this “heterogeneous” liquid structure may impact its physical and thermodynamic properties and associated applications in carbon capture and green solvent.
Abstract

Layer-structured LiCoO$_2$ is used as cathode material in lithium-ion batteries, which are widely used in mobile equipment such as cellular phones and laptop computers. In LiCoO$_2$, Li migration is highly anisotropic with Li transport along the crystallographic c-axis blocked by the CoO$_2$ layers. Therefore, in conventional lithium-ion batteries vertical electrodes have been used for Li charge-discharge cycles. Grain-boundary engineering would provide an additional pathway for Li transport and allows horizontal contact to be employed. The horizontal contact configuration also makes strain engineering possible to optimize Li transport by tuning epitaxial strain on LiCoO$_2$ films. In this work, using ab initio simulations and thermodynamics we investigate formation mechanism of domain boundaries, their relative stability, and defects at the antiphase boundary. We found that glide reflection symmetry of adjacent domains with respect to a vertical plane is critical for formation a vertical pathway for Li diffusion. Moreover, relative stability of the grain boundaries shows periodic pattern along the c-axis and antiphase boundary is one of energetically favorable structures. We found that the antisite defect with a Li atom at a Co site can be formed at very low energy cost or spontaneously at the antiphase boundary. These results show that grain-boundary engineering can open a viable pathway to enhance and optimize Li transport in LiCoO$_2$ films.
ZnS thin films are being investigated in thin film solar cells because of the wide band gap. Currently, the main application for ZnS is as a buffer layer in Cu(In,Ga)Se₂ (CIGS) thin film solar cells because of its similarities to CdS, the material most commonly used for this application. Cadmium free buffer and window layers are of particular interest due to the environmental toxicity of cadmium. Therefore, the focus of this work is the growth kinetics of an ammonia free chemical solution deposition for thin film ZnS. Chemical bath deposition using zinc sulfate, thioacetaamine (TAA), and nitrilotriacetic acid trisodium salt (Na₃NTA) to create ZnS thin films. In this study, activation energy, kinetic reaction rate and supersaturation were determined for the reaction. In-situ characterization of the film thickness and growth rate based on different bath conditions was measured using a quartz crystal microbalance. The kinetic study of the ZnS growth as a function of temperature, pH and precursor concentrations indicated the activation energy was 36.32 kJ/mol and lead to an empirical equation of ZnS growth rate for optimizing the batch reaction. The critical supersaturation was found to be 13 by analyzing the reaction mechanism and locating the start point of the growth region through SEM and TEM images. From this critical supersaturation, the critical size of ZnS stable nucleus can be defined as 13.8 nm which could be used in the future studies of either homogeneous or heterogeneous reaction. The morphology, composition and crystallinity of ZnS thin film were characterized by scanning electron microscopy, transmission electron microscopy, and energy dispersive X-ray spectroscopy. The optical band gap of ZnS thin film was 3.513 eV.
High-Voltage Nanolaminate Metal-Insulator-Metal (MIIM) Tunnel Diodes using ALD Al₂O₃ and Ta₂O₅
D.Z. Austin, M.A. Jenkins, K. Holden, J.F. Conley, Jr.*
School of ECECS, Oregon State University, Corvallis, OR, *jconley@ececs.oregonstate.edu

Atomic layer deposited (ALD) nanolaminate tunnel barriers have enabled enhancements of low voltage asymmetry ($\eta_{asym} = I_+/I_-$) and non-linearity ($f_{NL}$) in MIIM tunnel diodes for applications such as rectenna based energy harvesting.¹ ² In this work, we investigate ALD bi-layers of Al₂O₃ and Ta₂O₅ for high-voltage applications such as antenna diodes for plasma-induced damage protection and high-voltage one-time programmable non-volatile memory logic.

Nanolaminate Al₂O₃/Ta₂O₅ stacks were deposited on TaN bottom electrodes via ALD. ALD was performed at 200°C in a Picosun R-150 without breaking vacuum using alternating pulses of H₂ and either trimethylaluminum or tris(ethylmethylamido)(tert-butylimido)tantalum. Ta₂O₅:Al₂O₃ thickness ratios of 1:1, 2:1, 3:1, 5:1, and 9:1 were fabricated with the Al₂O₃ thickness fixed at 30 nm. Bias was applied to Al top electrodes formed by evaporation through a shadow mask.

I-V behavior (Fig. 1) was found to be a strong function of the Ta₂O₅:Al₂O₃ thickness ratio. Under positive bias, the reverse diode current for all devices remains low until the Al₂O₃ layer breaks down, at which point the current increases rapidly. This reverse Al₂O₃ breakdown voltage is controlled by the thickness of the Ta₂O₅ layer, occurring at 20 V for the 1:1 ratio to 67 V for the 1:9 ratio. For small magnitude negative bias, in the range of 0 to -15 V, the diode forward current is higher for thicker Ta₂O₅ layers, a somewhat counter-intuitive result. Beyond -15 V, the forward current is lower for thicker Ta₂O₅ layers, in line with expectations. The maximum asymmetry ratio and voltage are tuned by the Ta₂O₅ thickness, increasing from ~10³ at ~19 V for the 1:1 ratio to ~10⁵ at ~52 V for the 1:9 ratio. A detailed explanation of these results will be given at the meeting.

This work demonstrates that ALD bilayers may be used to effectively engineer the reverse breakdown voltage, maximum asymmetry, and operating range of high voltage MIIM diodes. These diodes may be of interest for implementation as back end of line devices as well as for large area electronics due to low temperature fabrication.

U3: Interaction of Butyltin \(\beta\)-Keggin Nanoclusters on Mica Substrates

D.R. Goddard,\(^1\) J.J. Hebert,\(^1\) J.T. Diulus,\(^1\) R.T. Frederick,\(^1\) J. Bergevin,\(^1\) D. Hutchison,\(^2\) M.R. Olsen,\(^2\) M. Nyman,\(^2\) G.S. Herman\(^{1,2}\)

\(^1\) School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR
\(^2\) Department of Chemistry, Oregon State University, Corvallis, OR

Moore’s law states that the number of transistors will double every two years. To achieve these high transistor densities the fundamental feature sizes are approaching the nanometer scale (sub-10 nm). The microelectronics industry is transitioning to extreme ultraviolet (EUV) photolithography to obtain very high resolution patterning, which is enabled by short wavelength (13.5 nm) photons. Organotin photoresists have high sensitivity to EUV photons compared to more common polymer-based resists. This new class of photoresists are synthesized to form high-uniformity, sub-nanometer clusters, which allow low line edge roughness and nanoscale features. Cluster/substrate interactions strongly influence the ability to form uniform films. In this presentation, we are investigating the interaction between the organotin clusters and mica substrates. For these studies a charge-neutral butyl tin (BuSn) cluster, \(\text{NaO}_4(\text{BuSn})_{12}(\text{OH})_3(O)(\text{OCH}_3)_{12}(	ext{Sn(H}_2\text{O})_2)\) (\(\beta\)-\(\text{NaSn}_{13}\)), was deposited onto a mica surface. To characterize the interaction of \(\beta\)-\(\text{NaSn}_{13}\) with mica surfaces, we dissolved \(\beta\)-\(\text{NaSn}_{13}\) in 2-heptanone and drop cast these solutions on freshly cleaved mica surfaces. We have investigated 1x10\(^{-3}\) M, 1x10\(^{-4}\) M, 1x10\(^{-5}\) M, and 1x10\(^{-6}\) M solutions. Atomic force microscopy (AFM) was used to characterize cluster/substrate interactions. AFM images indicated that agglomerated clusters had larger heights and diameters for solutions with higher concentrations. For the lowest concentrations, we found agglomerated clusters distributed across the mica surface. Increasing the solution concentration to 10\(^{-4}\) M led to an increase in the number of agglomerated clusters, but also resulted in regions with the partial formation of a cluster-based films. At the highest concentration (10\(^{-3}\) M) fully formed cluster-based films were obtained.
There has been an increased interest in using organometallic clusters for high-resolution patterning applications in the microelectronics industry. Organotin clusters have been used as inorganic resists for extreme ultraviolet (EUV) lithography. These materials have high sensitivity to EUV radiation and allow low line edge roughness to be achieved. These organotin clusters have the potential to allow formation of high resolution nanopatterns, which is necessary for the production of next generation electronics. We have recently demonstrated the synthesis and characterization of sodium templated butyltin (BuSn) β-Keggin clusters (β-NaSn\(_{13}\)), with the molecular formula NaO\(_4\)(BuSn)\(_{12}\)(OH)\(_3\)(O)\(_6\)(OCH\(_3\))\(_{12}\)(Sn(H\(_2\)O)\(_2\)), which can be used as a model organotin EUV resist. For these studies, β-NaSn\(_{13}\) was dissolved in 2-heptanone and drop casted on highly ordered pyrolytic graphite (HOPG). HOPG offers unique surface sites, such as step edges of varying layer height, which provide a range of sites where clusters can bind to the substrate. Atomic force microscopy (AFM) was used to analyze the morphology of β-NaSn\(_{13}\) features for depositions using 1×10\(^{-3}\) M, 1×10\(^{-4}\) M, 1×10\(^{-5}\) M, and 1×10\(^{-6}\) M solutions. AFM images allow for quantitative characterization of the size, shape, thickness, and preferred binding sites of clusters for solutions at each concentration. Height and diameter distributions of the agglomerated clusters was made using a statistical analysis of five images per sample for four samples. It was determined that as the concentration of cluster precursor solution increased, the height and diameter of agglomerated clusters increased until ~1×10\(^{-4}\) M. At 1×10\(^{-4}\) M the formation of a cluster-based film was observed, and for 1×10\(^{-3}\) M the cluster-based film appears to be uniformly distributed across the HOPG surface.
One method to improve condensation processes currently used in applications from thermal management to distillation is to utilize advanced condensing surfaces. It has been shown that superhydrophobic surfaces used for this purpose offer energy efficiencies an order of magnitude greater than their hydrophilic counterparts, but the latter generally sheds water with greater ease. The use of patterned surfaces made with nanostructured CuO thin films is investigated in this project. The films were created using Microreactor Assisted Nanomaterial Deposition system, followed by using a PDMS channel to coat thin film substrates. By using a reactor to create a precursor that is selectively flowed over a substrate, custom patterns can be created with the hope of creating surfaces with condensation efficiencies greater than either hydrophilic or hydrophobic surfaces alone. The effect on the CuO morphology by changing variables in the deposition process has been explored.