TWENTY-SEVENTH ANNUAL SYMPOSIUM

of the

LABORATORY FOR SURFACE MODIFICATION

Friday, March 8, 2013

8:30 a.m. to 5:30 p.m.

Rutgers, the State University of New Jersey

FINAL PROGRAM

Fiber Optics Auditorium
Busch Campus
Piscataway, New Jersey
TWENTY-SEVENTH ANNUAL SYMPOSIUM
LABORATORY FOR SURFACE MODIFICATION

8:15  Registration, coffee

8:30  Introductory Remarks
Professor Robert A. Bartynski,
Director, Laboratory for Surface Modification

SESSION I:
TOPOLOGICAL INSULATORS AND NANOMATERIALS FOR CLEAN ENERGY
Chair: Prof. Leonard Feldman
VP Physical Science and Engineering Partnerships
Director, IAMDN

8:48  In Diffusion in In$_2$Se$_3$/Bi$_2$Se$_3$: Correlation between Structure and Transport Properties
Can Xu*, Hang Dong Lee, Samir Shubeita, Matthew Brahlek, Nikesh Koirala, Seongshik Oh and Torgny Gustafsson
Department of Physics and Astronomy, and Laboratory for Surface Modification

9:00  Bulk-Insulating Bi$_2$Se$_3$ Thin Films and Decoupled Topological Surface States
Matthew Brahlek*¹, Nikesh Koirala¹, Namrata Bansal² and Seongshik Oh¹
¹Department of Physics & Astronomy and ²Department of Electrical and Computer Engineering

9:12  Engineering Quantum Anomalous Hall (QAH) Phases with Orbital and Spin Degrees of Freedom
Hongbing Zhang¹,², Frank Freimuth², Gustav Bihlmayer², Stefan Blügel², Marjana Lezaic², Yuriy Mokrousov¹ and David Vanderbilt¹
¹Department of Physics and Astronomy, and Laboratory for Surface Modification, and ²Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, German

9:24  Lithiation of UHV-prepared CoO Conversion Battery Materials Studied by XPS and TEM
Ryan Thorpe*¹, Sylvie Rangan¹, Robert A. Bartynski¹, Mahsa Sina², and Frederic Cosandey²
¹Department of Physics & Astronomy, and Laboratory for Surface Modification and ²Department of Materials Science and Engineering

9:36  Conversion Reaction Mechanisms in Lithiated/Delithiated FeO$_{0.7}$F$_{1.3}$/C Nanocomposite Battery Materials
Mahsa Sina¹, Nathalie Pereira¹,², Glenn G. Amatucci¹,² and Fred Cosandey¹
¹Department of Materials Science and Engineering and ²Energy Storage Research Group

9:48  Energy Alignment at Organic/Oxide and Organic/Metal Interfaces: The Effects of Molecular Overlayer Thickness on the HOMO/LUMO Gap and Interfacial Dipole
Charles Ruggieri*, Sylvie Rangan, Senia Coh and Robert A. Bartynski
Department of Physics and Astronomy, and Laboratory for Surface Modification

☕ 10:00 – 10:28 Coffee Break and Poster Session ☕

* = Student Presenter
SESSION II:
SURFACES AND NANOMATERIALS IN CATALYSIS
Chair: Prof. Charles Dismukes
Department of Chemistry and Chemical Biology
Rutgers Catalysis Research Center

Anandarup Goswami¹,², Sayantani Das¹,², Nagarajan Murali¹,² and Tewodros Asefa¹,²,³
¹Department of Chemistry and Chemical Biology, ²Department of Chemical and Biochemical Engineering, ³Institute for Advanced Materials, Devices and Nanotechnology

10:40 Proton Behavior at Glass/Water Interfaces: Implications on Reactions and Proton Transport
Stephen H. Garofalini and Glenn K. Lockwood
Interfacial Molecular Science Laboratory, Department of Materials Science and Engineering

10:52 Rational Design and Synthesis of Efficient Functional Nanomaterials for Electrocatalysis
Rafael Silva*¹ and Tewodros Asefa¹,²
¹Department of Chemistry and Chemical Biology and ²Department of Chemical and Biochemical Engineering

11:04 **HIGHLIGHT PRESENTATION**
Using Model Surfaces to Design Catalysts and Electrocatalysts
Jingguang G. Chen
Thayer Lindsley Professor of Chemical Engineering
Columbia University

12:04 – 1:12 Lunch and Poster Session

* = Student Presenter
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## POSTER PAPERS:

1) **Surface Studies of Ionic Liquid Thin Films**  
Aleksandra B. Biedron*¹,³, Tianyi Liu¹, Edward W. Castner, Jr.¹ and Eric L. Garfunkel¹,²  
¹Department of Chemistry and Chemical Biology, ²Department of Physics and  
Astronomy, and Laboratory for Surface Modification and ³Nanotechnology for Clean  
Energy IGERT

2) **Photoresist Activation and Degradation of EUV Optics**  
Boris Yakshinskiy and Robert Bartynski  
Department of Physics and Astronomy, and Laboratory for Surface Modification

3) **Phase Transformation in Lithiated FeOₓFᵧ Thin Films**  
Bryan Byles*,¹, Nathalie Pereira², Glenn G. Amatucci² and Fred Cosandey¹  
¹Institute for Advanced Materials, Devices and Nanotechnology and ²Energy Storage  
Research Group

4) **New Approaches in the Employment of Carbon Nanomaterials in the**  
**Development of Miniaturized Biosensors**  
Cecilia C. C Silva*,¹,², Rajesh Kappera², Lauro. T. Kubota¹ and Manish Chhowalla²  
¹Institute of Chemistry, University of Campinas (UNICAMP), Campinas, SP, Brazil and  
²Department of Materials Science and Engineering

5) **Photon-Mediated Reaction of Oxygen with Single Crystal Rubrene**  
Daniel Mastrogiovanni*,¹, Alan S. Wan², Samir Shubeita³,⁴, Vitaly Podzorov³,⁴, Leonard  
C. Feldman³,⁴ and Eric Garfunkel¹,⁴  
¹Department of Chemistry and Chemical Biology, ²Evans Analytical Group, New Jersey,  
³Department of Physics and Astronomy, and Laboratory for Surface Modification and  
⁴Institute for Advanced Materials, Devices and Nanotechnology

6) **SiC(4-H)/Dielectric Interface Characterization**  
Gang Liu*,¹,³, Yi Xu², Ayayi C. Ahyi⁴, Tamara Isaacs-Smith⁴, John R. Williams⁴, Eric  
Garfunkel²,³ and Leonard C. Feldman¹  
¹Institute for Advanced Materials, Devices, and Nanotechnology, ²Chemistry and  
Chemical Biology, ³Electrical and Computer Engineering, ⁴Department of Physics,  
Auburn University

7) **Catalytic Water Oxidation at Practical Operating Current Densities: A**  
**Comparison of Earth-Abundant Oxides vs. Rare Noble Metal Oxides**  
Graeme P. Gardner*, Clyde Cady, Martha Greenblatt and G. Charles Dismukes  
Department of Chemistry and Chemical Biology

8) **Melting Gel Films for Low Temperature Seals**  
Lisa C. Klein*,¹, Mihaela Jitianu¹ and Andrei Jitianu²  
¹Department of Chemistry, William Paterson University, ²Department of  
Chemistry, Lehman College, CUNY, ³Department of Materials Science and  
Engineering
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9) **Electronic and Catalytic Properties of Chemically Exfoliated Molybdenum Disulfide**
Maryam Salehi\(^*\), Damien Voiry\(^1\), Goki Eda\(^2\), Keivan Esfariani\(^3\) and Manish Chhowalla\(^1\)
\(^1\)Department of Materials Science and Engineering, \(^2\)Department of Physics, National University of Singapore, Singapore and \(^3\)Department of Mechanical and Aerospace Engineering

10) **The Highly Polarized Surface of Magnetoelectric Antiferromagnet**
Ning Wu\(^*\)\(^1,2\), Xi He\(^1\), Christian Binek\(^1\) and Peter A. Dowben\(^1\)
\(^1\)Department of Physics & Astronomy and the Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588-0111, USA and \(^2\)Institute for Advanced Materials, Devices and Nanotechnology

11) **What Determines Functionality in Water Oxidation Catalysis? Permutations of Ligand and Nuclearity on Discrete Cobalt Clusters**
Paul F. Smith\(^*\), Christopher Kaplan, Nicholas McCool, David M. Robinson, Nicholas Mezle, John E. Sheats and G. Charles Dismukes
Department of Chemistry and Chemical Biology

12) **The Nion UltraSTEM with 10 meV Electron Energy Loss Spectroscopy**
Philip E. Batson and Maureen J. Lagos
Institute for Advanced Materials, Devices and Nanotechnology

13) **Solution Processed Transition Metal Oxide Thin Films**
Rajesh Kappera\(^*\)\(^1\), Damien Voiry\(^1\), Diego Alves\(^1\), Muharrem Acerce\(^1\), Hisato Yamaguchi\(^1\), Sylvie Rangan\(^2\), Robert Bartynski\(^2\) and Manish Chhowalla\(^1\)
\(^1\)Materials Science and Engineering Department and \(^2\)Department of Physics and Astronomy, and Laboratory for Surface Modification

14) **Rutherford Backscattering Spectrometry Analysis of Brain Tissue Implanted with Ag Nanoparticles**
Samir Shubeita\(^*\)\(^1\), Hang Dong Lee\(^2\), Can Xu\(^2\), Damon Barbacci\(^3\), Amina Woods\(^3\), Albert Schultz\(^2\), Leszek Wielunski\(^2\), Torgny Gustafsson\(^2\) and Leonard C. Feldman\(^1\)
\(^1\)Institute for Advanced Materials, Devices and Nanotechnology, \(^2\)Department of Physics and Astronomy, and Laboratory for Surface Modification, \(^3\)NIDA-IRP, Baltimore, MD and \(^4\)Ionwerks Inc., Houston, TX

15) **First-Principles Calculations of Epitaxially Strained PbZrO\(_3\): Coexistence of Antiferroelectricity and Ferroelectricity**
Sebastian E. Reyes-Lillo\(^*\) and Karin M. Rabe
Department of Physics and Astronomy, and Laboratory for Surface Modification

16) **Interfacial Bonding and Morphological Control of Electrodeposited Polythiophene and ZnO**
Wenchun Feng\(^*\) and Eric Garfunkel
Department of Chemistry and Chemical Biology

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17) TPD and DFT Studies of Adsorption and Desorption of H$_2$ on Planar and Faceted Ir(210)
Wenhua Chen$^1$, Payam Kaghazchi$^2$, Timo Jacob$^2$ and Robert A. Bartynski$^1$
$^1$Department of Physics and Astronomy, and Laboratory for Surface Modification and $^2$Institut für Elektrochemie, Universität Ulm, Germany

18) Reduction of NO by C$_2$H$_2$ on Planar and Faceted Ir(210)
Wenhua Chen, Quantong Shen and Robert A. Bartynski
Department of Physics and Astronomy, and Laboratory for Surface Modification

19) Study of Interfacial Nitrogen at the 4H-SiC/SiO$_2$ and Si/SiO$_2$ Interface
Yi Xu$^{1,2}$, Gang Liu$^3$, Hang Dong Lee$^4$, Blair R. Tuttle$^5$, Sokrates T. Pantelides$^5$, John Williams$^6$, Sarit Dhar$^6$, Torgny Gustafsson$^6$, Eric Garfunkel$^{1,2}$ and Leonard C. Feldman$^{1,6}$
$^1$Department of Chemistry and Chemical Biology, $^2$Institite for Advanced Materials, Devices and Nanotechnology, $^3$Department of Electrical and Computer Engineering, $^4$Department of Physics and Astronomy, and Laboratory for Surface Modification, $^5$Department of Physics, Auburn University and $^6$Department of Physics and Astronomy, Vanderbilt University

20) Development of Inorganic-Organic Crystalline Hybrid Materials for Energy Related Applications
Xiao Zhang$^*$, Mojgan Roushan, Haohan Wu, Zhijuan Zhang, Jingming Zhang, Sanhita Pramanik and Jing Li
Department of Chemistry

21) Molecular Design and Dipole Effects at Semiconductor
Alberto Batarseh$^{1,*}$, Keyur Chitre$^1$, Andrew Kopecky$^1$, Elena Galoppini$^1$, Sylvie Rangan$^2$ and Robert A. Bartynski$^2$
$^1$Chemistry Department, Rutgers University, Newark and $^2$Department of Physics and Astronomy, and Laboratory for Surface Modification

22) Scanning Tunneling Microscopy Observations of Zinc Tetraphenylporphyrin Molecules on Au(111) Surface: Packing Geometry and Substrate Interactions
Charles Ruggieri$^{1,*}$, Sylvie Rangan and Robert A. Bartynski
Department of Physics and Astronomy, and Laboratory for Surface Modification

23) Binding Affinities of Iodine to Ruthenium Dyes
Hao Tang$^{1,*}$, Andrew Kopecky and Elena Galoppini
Department of Chemistry, Rutgers University, Newark

24) Ultrafast Proton Coupled Electron Transfer (PCET) in UVA and UVB Absorbers
Donald Prettypaul$^{1,*}$, Jianhua Bao and Piotr Piotrowiak
Department of Chemistry, Rutgers University, Newark

* = Student Presenter
25) **Excitons and Excess Electrons in Nanometer Size Polyoxotitanate Clusters: Electronic Spectra, Exciton Dynamics and Surface States**  
Jianhua Bao*, Zhihao Yu¹, Lars Gundlach¹, Jason B. Benedict², Philip Coppens², Hung Cheng Chen³, John R. Miller³ and Piotr Piotrowiak¹  
¹Department of Chemistry, Rutgers University, Newark, ²Department of Chemistry, University at Buffalo, ³Chemistry Department, Brookhaven National Laboratory

26) **Functionalization of Nanostructured ZnO Films by Copper-Free Click Reaction**  
Yan Cao*, Elena Galoppini¹, Pavel Ivanoff Reyes² and Yicheng Lu²  
¹Department of Chemistry, Rutgers University, Newark and ²Department of Electrical and Computer Engineering

27) **Molecular Mechanisms of the Conversion Reaction in FeF₂ Cathodes Exposed to Li in High Capacity Batteries**  
Ying Ma* and Stephen H. Garofalini  
Interfacial Molecular Science Laboratory, Department of Materials Science and Engineering

28) **Topological Phase Transitions in In- and Sb-doped Bi₂Se₃**  
Jianpeng Liu* and David Vanderbilt  
Department of Physics and Astronomy, and Laboratory for Surface Modification

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SESSION III:
COMPLEX MATERIALS: NOVEL PROPERTIES AND DEVICE IMPLICATIONS
Chair: Prof. Ronald Ransome
Department of Physics and Astronomy

1:12  Bloch-Type Ferroelectric Domain Walls in Rhombohedral BaTiO₃
Maryam Taherinejad¹, David Vanderbilt¹, Jiri Hlinka² and Vilgelmina Stepkova²
¹Department of Physics and Astronomy and ²Institute of Physics, Academy of Sciences of
the Czech Republic, Na Slovance, 18221 Praha, Czech Republic

1:24  Is Hexagonal InMnO₃ Ferroelectric?
Fei-Ting Huang¹, Xueyun Wang¹, Yoon Seok Oh¹, Kosuke Kurushima², Shigeo
Mori², Yoichi Horibe¹ and Sang-Wook Cheong¹
¹Institute Rutgers Center for Emergent Materials, ²Toray Research Center, Ohtsu,
Japan and ³Department of Materials Science, Osaka Prefecture University, Osaka,
Japan

1:36  Singlet Pairing on and Antiferromagnetic Background in CaMn₂Sb₂
Verner K. Thorsmølle¹, Alexander Ignatov¹, Maria E. Pezzoli¹,², Kristjan Haule¹, David
Kolchmeyer¹, Jack W. Simonson², Megan C. Aronson²,³ and Girsh Blumberg¹
¹Department of Physics and Astronomy, ²Department of Physics and Astronomy, Stony
Brook University and ³Condensed Matter Physics & Materials Science Department,
Brookhaven National Laboratory

1:48  Novel MgₓZn₁₋ₓO (0 ≤ x ≤ 0.06) TFT Technology
Chieh-Jen Ku*, Wen-Chiang Hong, Rui Li and Yicheng Lu
Department of Electrical and Computer Engineering

2:00  **HIGHLIGHT PRESENTATION**

Oxides as Complex Systems
Shriram Ramanathan
Harvard University, Cambridge

* = Student Presenter

3:00 – 3:24 Afternoon Break and Poster Session
SESSION IV:
NOVEL NANOMATERIALS AND BIOINTERFACES
Chair: Prof. Richard Lehman
Department of Materials Science and Engineering

3:24 Semi-Classical Models to Design Materials with High Thermoelectric Performance
Mona Zebarjadi
*Department of Mechanical and Aerospace Engineering

3:36 Thermal Transport from First-Principles
Keivan Esfarjani
Department of Mechanical and Aerospace Engineering

3:48 Capillary-Induced Interactions Between Janus Particles at Liquid-Fluid Interfaces
Hossein Rezvantalab* and Shahab Shojaei-Zadeh
*Department of Mechanical and Aerospace Engineering

4:00 Biophysical Characterization of the Interaction of Amphiphilic Macromolecules (AM) with Lipid Bilayers: Modeling the Role of AM Core Structure and Composition
Adriana A.T. Martin*, Michael Tomassini, Vladyslav Kholodovych, Sven Sommerfield, Kathryn E. Uhrich, William Welsh, Sanjeeva Murthy and Prabhas V. Moghe
1Department of Cellular and Molecular Pharmacology, University of Medicine and Dentistry of New Jersey-Robert Wood Johnson Medical School, 2Department of Biomedical Engineering, 3Department of Chemical and Biochemical Engineering, 4New Jersey Center for Biomaterials and 5Department of Chemistry and Chemical Biology

4:12 Gold Nanoparticle Dimers for SERS-Based Tissue Imaging
Swarnapali Indrasekara*, Bryan Paladini, Dominik Naczynski, Prabahs Moghe and Laura Fabris
1Department of Materials Science and Engineering, 2Department of Biomedical Engineering, 3Institute for Advanced Materials Devices and Nanotechnology

4:24 Temperature Effect On SiC Layer Exfoliation
Voshadhi P. Amarasinghe*, Leszek Wielunski, Adam Barcz, Leonard C. Feldman and George K. Celler
1Institute for Advanced Materials, Devices, and Nanotechnology, 2Department of Materials Science and Engineering, 3Department of Physics, 4Department of Chemistry and 5Institute of Electron Technology/Institute of Physics PAS, Warsaw, Poland

4:36 Low-Pressure Flame-Synthesized Carbon-Doped TiO₂ Nanoparticles
Hadi Halim*, Bernard H. Kear and Stephen D. Tse
*Department of Mechanical and Aerospace Engineering and 2Department of Materials Science and Engineering

4:48 End of Technical Presentations

4:55 Presentation of Theodore E. Madey Student Awards:
Best Poster Presentation
Best Oral Presentation

* = Student Presenter
ABSTRACTS FOR TALKS

8:48  In Diffusion in In$_2$Se$_3$/Bi$_2$Se$_3$: Correlation between Structure and Transport Properties
Can Xu*, Hang Dong Lee, Samir Shubeita, Matthew Brahlek, Nikesh Koirala, Seongshik Oh and Torgny Gustafsson
Department of Physics and Astronomy, and Laboratory for Surface Modification

The structure and chemical compatibility of In$_2$Se$_3$ (a band insulator) and Bi$_2$Se$_3$ (a 3D topological insulator) suggests possible promising applications of In$_2$Se$_3$/Bi$_2$Se$_3$ devices. Indiffusion of In into Bi$_2$Se$_3$ will affect the transport properties. We have grown In$_2$Se$_3$/Bi$_2$Se$_3$ thin films on sapphire by Molecular Beam Epitaxy at different temperatures. Our Medium Energy Ion Scattering data show that higher growth temperature increases In diffusion while the Bi$_2$Se$_3$ mobility decreases.

9:00  Bulk-Insulating Bi$_2$Se$_3$ Thin Films and Decoupled Topological Surface States
Matthew Brahlek*, Nikesh Koirala, Namrata Bansal and Seongshik Oh
1Department of Physics & Astronomy and 2Department of Electrical and Computer Engineering

Topological insulators (TI) are a new novel state of matter where a metallic surface band forms at the interface between two insulators which are described by different electronic topological invariants. The surface band formed at the interface has a linear Dirac-like dispersion, whose crossing is protected by time reversal symmetry, and therefore is robust under disorder. Despite the novel properties, the surface states have been shorted by a parallel bulk channel, and therefore have eluded direct probing by transport measurements. With the combination of thin molecular beam epitaxy grown Bi$_2$Se$_3$ films combined with compensation doping by Cu we present evidence for the first bulk-insulating samples. With this achieved, we found that the TI surface states on the top and the bottom of the film become coupled when the film thickness is below 10 nm, and can be fully decoupled for thickness above 20 nm.

9:12  Engineering Quantum Anomalous Hall (QAH) Phases with Orbital and Spin Degrees of Freedom
Hongbing Zhang*, Frank Freimuth, Gustav Bihlmayer, Stefan Blügel, Marjana Lezaic, Yurii Mokrousov and David Vanderbilt
1Department of Physics and Astronomy, and Laboratory for Surface Modification, and 2Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, German

Based on first-principles calculations, we demonstrate that under external exchange fields, non-zero Chern numbers and nontrivial QAH effects can be induced by on-site spin-orbit coupling in buckled honeycomb lattices with $sp$ orbitals, utilizing both orbital and spin degrees of freedom. We propose that Bi- or Sb(111) bilayers with ferromagnetic dopants are promising systems to achieve QAH effects.
9:24 Lithiation of UHV-prepared CoO Conversion Battery Materials Studied by XPS and TEM
Ryan Thorpe*, Sylvie Rangan¹, Robert A. Bartynski¹, Mahsa Sina², and Frederic Cosandey²
¹Department of Physics & Astronomy, and Laboratory for Surface Modification and
²Department of Materials Science and Engineering

CoO is a potential high-capacity Li-ion electrode material, undergoing a two-electron redox reaction in electrochemical cells. In order to study the fundamental electronic and structural changes that occur during discharge, we have grown 5nm epitaxial and polycrystalline CoO films and deposited atomic Li on the surface in UHV. When Li is deposited at 150°C, XPS shows consistent reduction of Co²⁺O directly to Co⁰ + Li₂O as a function of Li exposure with no intermediary phases, whereas at room temperature, a passivating Li₂O₂ surface layer inhibits the reaction. Epitaxial films show a higher degree of reactivity at both temperatures, possibly due to the presence of Li diffusion channels.

9:36 Conversion Reaction Mechanisms in Lithiated/Delithiated FeO₀.7F₁.₃/C Nanocomposite Battery Materials
Mahsa Sina*, Nathalie Pereira¹,², Glenn G. Amatucci¹,² and Fred Cosandey¹
¹Department of Materials Science and Engineering and ²Energy Storage Research Group

Iron oxyfluoride-carbon (FeOF/C) nanocomposites are been considered as alternative high energy density cathode material as they have a theoretical capacity in excess of 700 mAhg⁻¹. In contrast to intercalation compounds, which are limited to one electron transfer, FeOF/C converts to metallic Fe upon full discharge. At full conversion when all the valence states of Fe are used this corresponds to a maximum of three electrons transfer. In this study, the structural changes of FeOF/C during the first discharge-charge cycle at 60°C were studied by combined annular dark field (ADF) STEM, electron energy loss spectroscopy (EELS) and selected area electron diffraction (SAED) techniques. Simulations of SAED patterns for nanoparticles in the 2-4 nm range were obtained ab-initio using JEMS program. It was observed that upon lithiation to 1.5V, the FeOF/C nanocomposite converts to a nanocomposite mixture of Li-Fe-O-F rocksalt, LiF and metallic Fe. Upon full re-charging to 4.5V, the nanocomposite transforms back to a metastable rutile-rocksalt type structure with only short-range order. It is also found that this metastable phase mixture reconverts back to the original rutile structure under the electron beam.

* = Student Presenter
9:48 Energy Alignment at Organic/Oxide and Organic/Metal Interfaces: The Effects of Molecular Overlayer Thickness on the HOMO/LUMO Gap and Interfacial Dipole
Charles Ruggieri*, Sylvie Rangan, Senia Coh and Robert A. Bartynski
Department of Physics and Astronomy, and Laboratory for Surface Modification

Using direct and inverse photoemission, XPS, and STM we have investigated the electronic structure and bonding geometry of zinc tetraphenylporphyrin (ZnTPP) molecules adsorbed on a set of four oxide semiconductor and metallic substrates [TiO_2(110), ZnO(11-20), Ag(100) and Au(111)] at monolayer and multilayer coverages. The vacuum levels of the organic/oxide and organic/metal systems were also measured and the interface dipoles determined.

Anandarup Goswami¹², Sayantani Das¹², Nagarajan Murali¹² and Tewodros Asefa¹²,³
¹Department of Chemistry and Chemical Biology, ²Department of Chemical and Biochemical Engineering, ³Institute for Advanced Materials, Devices and Nanotechnology

The recent progress in heterogeneous catalysis specifically with mesoporous silica materials can be attributed to the controlled modulations of their physical and chemical properties using simpler strategies. However, despite their vast application in catalysis, the effect of mildly acidic surface silanol groups remains relatively unexplored. In this work, mesoporous silica SBA-15 with surface silanol groups was functionalized/grafted with t-amines and has been utilized in Michael reaction. The reaction was monitored using variable temperature NMR-kinetics that offers a direct measurement to the conversion. The effect of surface silanol groups and the recyclability of the catalyst have been studied.

10:40 Proton Behavior at Glass/Water Interfaces: Implications on Reactions and Proton Transport
Stephen H. Garofalini and Glenn K. Lockwood
Interfacial Molecular Science Laboratory, Department of Materials Science and Engineering

We developed a dissociative water potential that matches many properties of bulk water and the high thermal expansion of nanoconfined water and shows proton transport and hydronium ion lifetimes consistent with ab-initio calculations. We apply this potential to water/silica interfaces, showing details of these surface sites, their lifetimes and their effect on proton transport seen in electrochemical studies.

* = Student Presenter
Rational Design and Synthesis of Efficient Functional Nanomaterials for Electrocatalysis
Rafael Silva*¹ and Tewodros Asefa¹,²
³Department of Chemistry and Chemical Biology and ²Department of Chemical and Biochemical Engineering

Almost all energy related chemical transformations involve electrons transfer processes. The efficiency of these processes often relies on other chemical species or materials called “electrocatalysts” that are capable of mediating the electron transfer processes and/or stabilize the reactions’ transitions states. In this presentation, I will discuss our efforts using rational design and synthetic approaches to the development of new nanostructured electrocatalysts composed of noble-metal-free materials with high surface areas and specific heteroatom dopants and their use as electrocatalysts for the half-cell reactions within fuel cells. These materials were proven to be effective for electrons transfer processes pertinent to fuel cells or for potential renewable energy related applications such as the generation of electricity from fuels such as hydrogen in fuel cells.¹,² The structures and electrocatalytic properties of the materials as well as the interplay between their structures and properties were elucidated by various methods including TEM, XPS, SEM, various electrochemicals measurements, etc.

11:04 **HIGHLIGHT PRESENTATION**

**Using Model Surfaces to Design Catalysts and Electrocatalysts**

Jingguang G. Chen

*Thayer Lindsley Professor of Chemical Engineering*

*Columbia University*

In the current talk we will use two examples to demonstrate the importance of using surface science studies to identify catalysts and electrocatalysts. Our research approaches involve parallel efforts in density functional theory (DFT) calculations, surface science experiments on model systems, and synthesis and evaluation of supported catalysts under thermochemical or electrochemical conditions. We will first use water electrolysis to demonstrate the feasibility of using monolayer Pt on tungsten carbide (WC) to achieve the same activity as bulk Pt. We will present DFT calculations of similar electronic and chemical properties between monolayer Pt/WC and Pt, synthesis and characterization of monolayer Pt/WC films, and electrochemical evaluation of the activity and stability of Pt/WC for water electrolysis. Comparing to the leading Pt electrocatalyst, the monolayer Pt/WC represents a significant reduction in Pt loading in electrolyzers and photoelectrochemical devices [1-3].

We will then use the conversion of biomass-derived oxygenates to illustrate the advantages of using bimetallic catalysts. Bimetallic catalysts often show unique activity and selectivity over their parent metals due to the electronic modification and strain effect [4,5]. We will present our results on the characterization of Ni/Pt bimetallic surfaces and catalysts under in-situ reaction conditions, further highlighting the importance of using the combined approaches of DFT calculations, surface science experiments, and reactor evaluations [6,7].

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* = Student Presenter
1:12 Bloch-Type Ferroelectric Domain Walls in Rhombohedral BaTiO₃
Maryam Taherinejad, David Vanderbilt, Jiri Hlinka and Vilgelmina Stepkova
1Department of Physics and Astronomy and 2Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance, 18221 Praha, Czech Republic

Ferroelectric domain walls (FDWs) are usually considered to be of Ising type, but there have been suggestions in recent years that Bloch-type FDWs, in which the polarization rotates in the plane of the FDW, are also possible. The mechanically compatible and electrically neutral FDWs in rhombohedral BaTiO₃ are of 71°, 109°, and 180° type. We have investigated these FDWs based both on first-principles calculations and on a Ginzburg-Landau-Devonshire (GLD) model [1]. The results from both approaches [2] confirm the Ising nature of the 71° FDW and the Bloch nature of the 180° FDW, and predict both Ising-type and Bloch-type FDWs are possible for the 109° case. Considering the relatively small rhombohedral strain in BaTiO₃, the competition between the energies of Bloch and Ising FDWs can be discussed in terms of a picture in which a Bloch wall is regarded as being composed of a pair of smaller-angle Ising ones. A reduction by 40% in the parameters describing the gradient term in the GLD model brings it into better agreement with the first-principles results for detailed properties such as the energies and widths of the FDWs.


1:24 Is Hexagonal InMnO₃ Ferroelectric?
Fei-Ting Huang, Xueyun Wang, Yoon Seok Oh, Kosuke Kurushima, Shigeo Mori, Yoichi Horibe and Sang-Wook Cheong
1Institute Rutgers Center for Emergent Materials, 2Toray Research Center, Ohtsu, Japan and 3Department of Materials Science, Osaka Prefecture University, Osaka, Japan

Hexagonal manganite (h-RE₃MnO₅; RE=rare earths) shows a unique improper ferroelectricity, accompanying a structural trimerization. RE can be replaced by In, which is much smaller than any RE ions. Recently, Oak et al. [1] suggested InMnO₃ is ferroelectric from the results of first-principles calculations, while Kumagai et al. [2] proposed a non-ferroelectric ground state. We will report the structural domains and local structural distortions of InMnO₃ using dark-field transmission electron microscopy. We demonstrate that InMnO₃ shows a distinct √3x√3-type superstructure from the paraelectric phase, and the domain structure can be delicately controlled by varying the thermal treatments.

1:36 Singlet Pairing on and Antiferromagnetic Background in CaMn$_2$Sb$_2$

Verner K. Thorsmølle$^1$, Alexander Ignatov$^1$, Maria E. Pezzoli$^{1,2}$, Kristjan Haule$^1$, David Kolchmeyer$^1$, Jack W. Simonson$^2$, Megan C. Aronson$^{2,3}$, and Girsh Blumberg$^1$

$^1$Department of Physics and Astronomy, $^2$Department of Physics and Astronomy, Stony Brook University and $^3$Condensed Matter Physics & Materials Science Department, Brookhaven National Laboratory

CaMn$_2$Sb$_2$ presents a magnetic system with a buckled hexagonal lattice of half-filled d-band Mn$^{2+}$ ions. AC resistivity and susceptibility exhibit non-monotonic temperature dependence in 85-200 K; a weak ferromagnetic phase below 200 K and an antiferromagnetic (AF) phase below 85 K. DFT+DMFT showing an average occupation of 5.1 for the d-orbitals is attributed to self-doping beyond half-filling arising from hybridization of Mn 3d and Sb p-bands. Raman spectroscopy shows a broad continuum below ~50 meV which below the AF transition emerges into a coherent excitation at 32 meV which governs Arrhenius type conductivity. We propose interpretation of these in-gap states in terms of bound disproportionate charge singlets.

1:48 Novel Mg$_x$Zn$_{1-x}$O (0 ≤ x ≤ 0.06) TFT Technology

Chieh-Jen Ku*, Wen-Chiang Hong, Rui Li and Yicheng Lu
Department of Electrical and Computer Engineering

We have demonstrated the new MZO (Mg$_x$Zn$_{1-x}$O , 0 < x ≤ 0.06) thin film transistor (TFT) technology by utilizing in-situ alloying of MgO and ZnO to form the ternary MZO as the TFT channel layer. The novel MZO TFTs feature superior electrical characters. In MZO TFTs, Mg$^{2+}$ ions are incorporated into ZnO to hinder the formation of oxygen vacancies in the TFT channel due to higher bonding energy of MgO than that of ZnO. The MZO TFT technology also offers the better thermal stability and the negative biasing stress (NBS) stability over the ZnO counterpart. The MZO TFT technology offers promising applications in large area electronic systems and flexible electronics, such as advanced displays and sensors.

2:00 **HIGHLIGHT PRESENTATION**

Oxides as Complex Systems

Shriram Ramanathan
Harvard University, Cambridge

We will discuss the structural, compositional and electronic complexity in oxides with particular emphasis on proximity to phase transitions. Two classes of transitions: electronic (such as metal-insulator) and electrochemical (such as ionic-electronic) and their synergies will be discussed. Experimental results on high-performance correlated electron system-based solid state devices for information processing and high frequency communications and their integration with silicon platforms will be presented. Unique opportunities and the possibility of emergent states with oxide heterostructures will then be considered. I will then discuss Little Robeep, an emerging program to realize embeddable two-dimensional solid oxide fuel cells for energy generation/storage for autonomous systems.
3:24 Semi-Classical Models to Design Materials with High Thermoelectric Performance
Mona Zebarjadi
Department of Mechanical and Aerospace Engineering

Modern thermoelectrics are mostly nanocomposites with many interfaces to reduce lattice thermal conductivity. Design of selective interfaces that can favor electron conduction and block phonon conduction at the same time can increase the thermoelectric figure of merit. In this talk I will discuss several models that has been developed to simulate electron and phonon transport across interfaces and nanoparticles. The understanding that was gained by these simulations were used to find new strategies to increase the performance of thermoelectric materials either by operating them under different conditions or by designing new structures with enhanced thermoelectric properties.

3:36 Thermal Transport from First-Principles
Keivan Esfarjani*
Department of Mechanical and Aerospace Engineering

The methodology we have developed to calculate thermal conductivity of crystalline solids from first-principles density-functional theory will first be described. The method has been applied to simple systems such as Si and GaAs as well less trivial ones such as ZrCoSb and PbTe which have applications as good thermoelectric materials.

Results will be discussed and compared to available experimental data. In particular, we will explain why PbTe has such a low thermal conductivity.

3:48 Capillary-Induced Interactions Between Janus Particles at Liquid-Fluid Interfaces
Hossein Rezvantalab* and Shahab Shojaei-Zadeh
Department of Mechanical and Aerospace Engineering

We study the capillary-induced interactions between Janus particles adsorbed at flat oil-water interfaces. The interface deforms around the particles due to surface heterogeneity and/or shape anisotropy, thus giving rise to energetic capillary-induced interactions. We quantify these interactions through evaluation of capillary energy variation as a function of the aspect ratio, amphiphilicity, separation distance and bond angle between the particles. We also discuss the preferred alignment and assembly of these particles into 1D chains. This study has practical implications for design of complex interfaces containing solid particles.
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4:00  Biophysical Characterization of the Interaction of Amphiphilic Macromolecules (AM) with Lipid Bilayers: Modeling the Role of AM Core Structure and Composition
Adriana A.T. Martin*, Michael Tomassini, Vladyslav Kholodovych, Sven Sommerfield, Kathryn E. Uhrich, William Welsh, Sanjeeva Murthy and Prabhas V. Moghe

Amphiphilic macromolecules (AM) have the potential to exhibit enhanced bioactivity by partitioning into cellular membranes. As the AM-membrane association mechanisms are not well understood, we conducted modeling studies based on coarse grained, computational molecular dynamics and experimental binding studies using Quartz crystal microbalance with dissipation (QCM-D). Both approaches confirmed that AMs with cores possessing varying charge, hydrophobicity, sugar structure and stereochemistry showed graded model membrane binding. Overall, specific AM features that promote membrane binding were identified, which can guide the application of AMs for tissue targeting and therapeutic applications.

4:12  Gold Nanoparticle Dimers for SERS-Based Tissue Imaging
Swarnapali Indrasekara, Bryan Paladini, Dominik Naczynski, Prabhas Moghe and Laura Fabris

Herein, a new class of nanoparticle platform is presented for surface enhanced Raman scattering (SERS)-based selective tissue detection. Controlled assembly of gold nanoparticles (Au NP) into dimers is achieved using a small, rigid Raman-active dithiolated linker molecule. Dimerization concurrently places the SERS reporter within the interparticle gap; the region of highest SERS enhancement. Dimers are functionalized with cancer cell targeting moieties and fluorescent tags to facilitate simultaneous tissue targeting and imaging respectively. SERS mapping of human glioblastoma cells treated with as-functionalized Au NP dimers show markedly enhanced signal intensity and detection limit compare to conventional confocal fluorescence microscopy. These results present Au NP dimers as a promising and versatile optical imaging tool for fast, selective, and ultrasensitive tissue targeting and disease detection, and screening.

4:24  Temperature Effect On SiC Layer Exfoliation
Voshadhi P. Amarasinghe, Leszek Wielunski, Adam Barcz, Leonard C. Feldman and George K. Celler

Hydrogen ion beam implantation-assisted exfoliation of single crystalline silicon carbide (SiC) is used to study the influence of ion implantation temperature on SiC layer transfer. From the five temperatures tested (liquid N2 cooled, RT, 250°C, 300°C, 600°C) it was observed that increasing implantation temperature to 300°C produced the most successful
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exfoliation. TRIM calculations, RBS, and SIMS data were used to find out the damage peak and the hydrogen concentration peaks. Anneal data were used to understand the efficiency of exfoliation with respect to each implantation temperature.

4:36 Low-Pressure Flame-Synthesized Carbon-Doped TiO$_2$ Nanoparticles

Hadi Halim$^*$, Bernard H. Kear$^2$ and Stephen D. Tse$^3$

$^1$Department of Mechanical and Aerospace Engineering and $^2$Department of Materials Science and Engineering

Carbon-doped TiO$_2$ nanoparticles of different phases are synthesized using a low pressure (20 torr) premixed flame in stagnation-point geometry. Hydrogen/ethylene mixture (1:1) serves as fuel, reacting stoichiometrically with oxygen, with nitrogen dilution. Titanium Tetra Iso-Propoxide (TTIP) precursor is injected to the flame. Results from XRD indicate different phases of TiO$_2$ such as rutile, anatase, and TiO$_2$-II, for different processing conditions. TEM shows that the primary particle sizes range from 3-7nm in diameter. XPS reveals that nanoparticles are carbon doped with Ti-O-C chemical structure. Finally, HRTEM and STEM-EELS analysis will be presented to elucidate the type of carbon doping in our TiO$_2$-carbon nano composite.

* = Student Presenter
1) **Surface Studies of Ionic Liquid Thin Films**  
Aleksandra B. Biedron*, Tianyi Liu¹, Edward W. Castner, Jr.¹ and Eric L. Garfunkel ¹,²  
¹Department of Chemistry and Chemical Biology, ²Department of Physics and Astronomy, and Laboratory for Surface Modification, and ³Nanotechnology for Clean Energy IGERT

Ionic liquids (ILs) have negligible vapor pressure, high conductivity, high viscosity, and good electrochemical stability. Ion layering and preferential orientations may be observed by varying the interfacial interactions at the solid-liquid interface. A set of four ILs has been studied; the set comprises with four different cations paired with the hydrophobic bis(trifluoromethylsulfonyl)amide anion. The set of cations includes one tetraalkylphosphonium and three dialkylimidazoliums. The ILs were spin coated on silicon substrates and film thickness was characterized using ellipsometry. Surface profiling was done using atomic force microscopy and X-ray photoelectron spectroscopy was utilized to estimate elemental composition and film thickness.

2) **Photoresist Activation and Degradation of EUV Optics**  
Boris Yakshinskiy and Robert Bartynski  
Department of Physics and Astronomy, and Laboratory for Surface Modification

The study of electron structure of polymers, aimed to clarify the photoresist activation mechanism existing in the Extreme-UV Lithography tools, is shown. On the other hand, the resist outgassing causes degradation of the EUV mirrors due to the irradiation-induced surface reactions resulting in the surface oxidation or carbonization. Deposition of protective layers including graphene can decrease a contamination rate of the mirror surface.

3) **Phase Transformation in Lithiated FeOₓFᵧ Thin Films**  
Bryan Byles*, Nathalie Pereira², Glenn G. Amatucci² and Fred Cosandey¹  
¹Institute for Advanced Materials, Devices and Nanotechnology and ²Energy Storage Research Group

With current Li-ion battery technologies reaching their intrinsic limit, new classes of materials have emerged based on conversion reactions. These conversion materials, such as FeOF, have higher capacity than conventional intercalation cathode materials. In order to produce FeOF, FeF₂ thin films were first deposited on thin carbon supports followed by oxidation to form FeOₓFᵧ thin films. These FeOₓFᵧ thin films were subsequently lithiated and studied with various TEM imaging techniques, nano-probe diffraction, and electron energy loss spectroscopy (EELS). It was found that varying degrees of lithiation had occurred and the extent of phase transformation was determined based on observed structure, Li content, and Fe valence state.
4) New Approaches in the Employment of Carbon Nanomaterials in the Development of Miniaturized Biosensors
Cecilia C. C Silva*,1,2, Rajesh Kappera2, Lauro. T. Kubota1 and Manish Chhowalla2
1Institute of Chemistry, University of Campinas (UNICAMP), Campinas, SP, Brazil and
2Department of Materials Science and Engineering

Carbon nanomaterials (CNTs and graphene) have been the center of attention for the development of advanced electric devices, mainly the field effect transistors (FETs). Because their electrical conductivity can be modified through interaction with chemical or biological species and as their dimensions are comparable to the analyte to be detected, these carbon nanomaterials based devices present a high electrical sensitivity. In this work, we report the independent and separated wafer-scale assembly of a high density of single-walled carbon nanotubes (SWCNTs) and graphene. In the following step, we explored their application in the development of arrays of devices based on FETs aiming to apply these devices as (bio)sensors to detect polyelectrolytes and cancer biomarkers.

5) Photon-Mediated Reaction of Oxygen with Single Crystal Rubrene
Daniel Mastrogiovanni*,1, Alan S. Wan5, Samir Shubeita3,4, Vitaly Podzorov3,4, Leonard C. Feldman1,3 and Eric Garfunkel1,4
1Department of Chemistry and Chemical Biology, 2Evans Analytical Group, New Jersey, 3Department of Physics and Astronomy, and Laboratory for Surface Modification and 4Institute for Advanced Materials, Devices and Nanotechnology

Single crystal rubrene is a model organic electronic material showing high carrier mobility and long exciton lifetime. These properties are detrimentally affected when rubrene is exposed to light under ambient conditions for prolonged periods of time. Using scanning probe microscopy and photoelectron, scanning probe, ion scattering, and mass spectrosopies we characterize the manner in which oxygen interacts with this material. We find that in the presence of light, oxygen penetrates into the bulk crystal by first reacting with molecules at step edges.

6) SiC(4-H)/Dielectric Interface Characterization
Gang Liu*,1,3, Yi Xu2, Ayayi C. Ahyi4, Tamara Isaacs-Smith4, John R. Williams4, Eric Garfunkel2,3, Sarit Dhar4 and Leonard C. Feldman1
1Institute for Advanced Materials, Devices, and Nanotechnology, 2Chemistry and Chemical Biology, 3Electrical and Computer Engineering, 4Department of Physics, Auburn University

Improvement in the quality of the SiO2/4H-SiC interface is vital for development of efficient SiC metal-oxide-semiconductor (MOS) technologies. For the Si-face, nitric oxide (NO) post-oxidation annealing is the most established interface passivation process which results in a field-effect mobility $\mu_{\text{FE}}$ of ~40 cm²/V-s, where interface trap coulomb scattering ($D_n$) was considered the main limiting factor. Phosphorus passivation was found more effective, resulting in ~125 cm²/V-s on a-face and ~80cm²/V-s on Si-face. Along with improved mobility, it is observed that $D_n$ is no longer the limiting factor. It is critical to identify new limiting mechanisms for better understanding and further improvement of mobility. Candidates include interfacial counter doping.

* = Student Presenter
7) Catalytic Water Oxidation at Practical Operating Current Densities: A Comparison of Earth-Abundant Oxides vs. Rare Noble Metal Oxides
Graeme P. Gardner*, Clyde Cady, Martha Greenblatt and G. Charles Dismukes
Department of Chemistry and Chemical Biology

Critical to the implementation of low-cost, earth-abundant catalysts for water splitting in commercial-scale electrolyzers is the demonstration that they can perform comparable to the current noble metal-based catalysts already in operation. The cubic polymorph of lithium cobalt oxide (LiCoO$_2$) acts as an excellent electrocatalyst for the water oxidation half-reaction. To demonstrate its performance, membrane electrode assemblies (MEAs) have been fabricated and tested in a rotating disk electrode (RDE) setup in pH 7 sodium sulfate/phosphate buffer, and pH 14 sodium hydroxide. As a benchmark, iridium (20% on carbon) was also tested under the same conditions with the same catalyst loading. Intrinsic activity was ascertained from onset potentials and Tafel analyses for both catalysts. Overall MEA stability and performance was tested by running at 10 mA/cm$^2$ for 2 hours while monitoring overpotential. The efficiency and stability of the costly, noble metal iridium is shown to be within the sight of the much more scalable, LiCoO$_2$.

8) Melting Gel Films for Low Temperature Seals
Lisa C. Klein*, Mihaela Jitianu$^1$ and Andrei Jitianu$^2$

$^1$Department of Chemistry, William Paterson University, $^2$Department of Chemistry, Lehman College, CUNY, $^3$Department of Materials Science and Engineering

Melting gels are silica-based hybrid nanocomposites with the curious behavior that they are rigid at room temperature, but soften around 110°C. A typical melting gel is prepared by mixing methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMDES), meaning one or two methyl groups are substituted for ethoxy. The methyl groups do not hydrolyze, which limits the network-forming capability of the precursors. To gain insight into the molecular structure of the melting gels, differential scanning calorimetry and oscillatory rheometry studies were performed. These measurements were made on melting gels before consolidation. The glass transition temperatures ($T_g$) obtained from both methods are in excellent agreement.
Electronic and Catalytic Properties of Chemically Exfoliated Molybdenum Disulfide
Maryam Salehi, Damien Voiry, Goki Eda, Keivan Esfarjani and Manish Chhowalla
Department of Materials Science and Engineering, Department of Physics, National University of Singapore, Singapore and Department of Mechanical and Aerospace Engineering

Molybdenum disulfide (MoS$_2$), a widely known Transition Metal Dichalcogenide (TMDs) having a layered structure, has recently attracted a great attention due to its novel optoelectronic and catalytic properties. The weak Van der Waals interaction between S-Mo-S layers makes it possible to exfoliate the crystal into individual layers. Recent studies on exfoliating LTMDs have shown dramatic changes of the optoelectronic properties when making these materials single-layer. For instance, the nature of indirect band gap for the bulk MoS$_2$ changes to direct gap for monolayer counterpart resulting in a huge enhancement (~10$^4$) in photoluminescence quantum yield. Being an attractive route for large-scale synthesis of single layer crystals, we have studied the chemical exfoliation of bulk MoS$_2$ via lithium intercalation. Both experimental and theoretical results for structural, electronic and catalytic properties of chemically exfoliated MoS$_2$ will be presented.


The Highly Polarized Surface of Magnetolectric Antiferromagnet
Ning Wu, Xi He, Christian Binek and Peter A. Dowben
Department of Physics & Astronomy and the Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588-0111, USA and Institute for Advanced Materials, Devices and Nanotechnology

Manipulation of magnetically ordered states by electrical means is among the most promising approaches towards novel spintronic devices. We have demonstrated that a very unusual high polarization with magnetic order exists at the surface of the Cr$_2$O$_3$ (0001) and is robust against surface roughness from SPUPS. Both magnetic single domain and multi-domains were imaged by MFM and XMCD-PEEM. Using a ferromagnetic Pd/Co multilayer deposited on top of Cr$_2$O$_3$ single crystal, we achieve reversible, room-temperature isothermal switching of the exchange-bias field, which reflects the switching of the bulk antiferromagnetic domain state and the interface boundary magnetization coupled to it.

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11) **What Determines Functionality in Water Oxidation Catalysis?**
**Permutations of Ligand and Nuclearity on Discrete Cobalt Clusters**  
**Paul F. Smith***, Christopher Kaplan, Nicholas McCool, David M. Robinson, Nicholas Mezle, John E. Sheats and G. Charles Dismukes  
*Department of Chemistry and Chemical Biology*

The metal-oxo \( \text{M}_4\text{O}_4 \) “cubane” topology is of great significance to the field of water oxidation as it represents the merging of bioinspired structural principles derived from natural photosynthesis with successful artificial catalysts known to date. The \( \text{Co}_4\text{O}_4 \) cubane is postulated to be the structural unit responsible for activity in a variety of heterogeneous catalysts (e.g., \( \text{LiCoO}_2 \) and \( \text{Co}_3\text{O}_4 \)); among the best evidence to support this is the finding that the discrete cluster \( \text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4 \) is a homogeneous catalyst.

For our first attempts at discerning the mechanism, we 1) directly compared the catalytic rates to those of the analog \([\text{Co}_4\text{O}_4(\text{OAc})_2(\text{bpy})_2]^{2+}\), and 2) isolated and tested “half cubane” \( \text{Co}_2\text{O}_2 \) and “incomplete cubane” \( \text{Co}_3\text{O}_{3.4} \) clusters within the same ligand sets. Our results demonstrate the requirement for four redox active Co atoms for catalytic activity. For the cubanes, a two fold increase in the \( \text{O}_2 \) evolution rate occurs upon replacing nonlabile N-donor ligands (Py) with labile OAc.

12) **The Nion UltraSTEM with 10 meV Electron Energy Loss Spectroscopy**  
**Philip E. Batson** and Maureen J. Lagos  
*Institute for Advanced Materials, Devices and Nanotechnology*

Spatially Resolved Electron Energy Loss Spectroscopy (EELS) at the 200-500 meV level in the electron microscope is a powerful technique for investigation of electronic properties in solids near defects and internal interfaces, and photonic and plasmonic band-structure in layered and aggregate materials, to name only a few. High Resolution EELS, using sub-10 eV beams a few tens of microns in diameter, has shown a wealth of surface information at terahertz through optical frequencies from carrier plasmons, phonons, and molecular vibrations. The new Nion Company's UltraSTEM electron microscope to be brought to Rutgers in the summer of 2013 will be the first instrument to combine atomic resolution imaging with an energy resolution of about 10 meV. At this energy resolution we will be able to measure sub-eV electronic and vibrational behavior of atomic to nanoscale sized structures. The planned research includes identifying different atomic and molecular species by their vibrational signatures at surfaces and buried interfaces, investigation of band-structure changes driven by quantum confinement, electronic behavior of defects, configuration changes in carbon based nanostructures, phonon instabilities within objects as they undergo size-driven structural changes, and low energy carrier plasmon behavior such as exists in graphene. Investigation of optical polarization fields, forces and particle movement under the electron beam may also shed light on molecular self-assembly driven by dispersion forces.

* = Student Presenter
13) **Solution Processed Transition Metal Oxide Thin Films**

Rajesh Kappera\(^1\), Damien Voiry\(^1\), Diego Alves\(^1\), Muharrem Acerce\(^1\),
Hisato Yamaguchi\(^1\), Sylvie Rangan\(^2\), Robert Bartynski\(^2\) and Manish Chhowalla\(^1\)
\(^1\)Materials Science and Engineering Department and \(^2\)Department of Physics and
Astronomy, and Laboratory for Surface Modification

Transition metal oxides (e.g. MoO\(_3\), WoO\(_3\)) have many interesting applications in
catalysis, smart windows, gas sensors, lubricants and so on. An efficient way of making
thin films of these oxides will be presented. Solution-processed films of single layer
MoS\(_2\) and WS\(_2\) are annealed in oxygen under controlled conditions to form layered MoO\(_3\)
and WO\(_3\). XPS, Raman and XRD confirmed the material’s composition and crystalline
structure. The electronic band structure was measured using ultra-violet photoemission
spectroscopy (UPS) and inverse photoemission spectroscopy (IPS). The Electrochromic
property of these films was studied and coloration/bleaching states were observed for
reduction and oxidation states.

14) **Rutherford Backscattering Spectrometry Analysis of Brain Tissue Implanted
with Ag Nanoparticles**

Samir Shubeita\(^1\), Hang Dong Lee\(^2\), Can Xu\(^2\), Damon Barbacci\(^3\), Amina Woods\(^3\),
Albert Schultz\(^2\), Leszek Wielunski\(^2\), Torgny Gustafsson\(^2\) and Leonard C. Feldman\(^1\)
\(^1\)Institute for Advanced Materials, Devices and Nanotechnology, \(^2\)Department of Physics
and Astronomy, and Laboratory for Surface Modification, \(^3\)NIDA-IRP, Baltimore, MD
and \(^4\)Ionwerks Inc., Houston, TX

The implantation of Au and Ag nanoparticles on tissues has shown promising results
when used as matrix on MALDI (Matrix Assisted Laser Desorption/Ionization) mass
spectrometry of biomolecules (e.g. proteins and lipids), instead of the usual organic
matrix. Nevertheless, non-uniform distribution of the implanted nanoparticles can lead to
misleading results of the local concentration of biomolecules as measured by MALDI.
We have used 2 MeV “He” Rutherford backscattering spectrometry to determine the Ag
atomic distribution on AgNP (5-7 nm diameters) implanted rat brain tissues. The results
show a good uniformity of the Ag atomic distribution in the tissue.

15) **First-Principles Calculations of Epitaxially Strained PbZrO\(_3\): Coexistence
of Antiferroelectricity and Ferroelectricity**

Sebastian E. Reyes-Lillo\(^*\) and Karin M. Rabe

Department of Physics and Astronomy, and Laboratory for Surface Modification

The antiferroelectric (AFE) - ferroelectric (FE) field-induced transition has important
applications in energy-storage capacitors and piezoelectric devices. PbZrO\(_3\) is the best
known AFE material. Polycrystalline and single crystals PbZrO\(_3\) possess a stable AFE
ground state below 505 K. In thin films, experimental results show coexistence of
antiferroelectricity and ferroelectricity at room and low temperatures. First-principles
calculations of epitaxially strained PbZrO\(_3\) are carried out to give further evidence of this
coexistence and to study the polarization switching path. The space groups of the AFE
and FE structures are identified together with their important structural and electrical
features.

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16) Interfacial Bonding and Morphological Control of Electrodeposited Polythiophene and ZnO
Wenchun Feng* and Eric Garfunkel
Department of Chemistry and Chemical Biology

Organic-inorganic hybrid solar cells have attracted considerable attention as a viable candidate for high efficiency photovoltaics. In this work, electrodeposited polythiophene (e-PT) was integrated with ZnO to produce hybrid solar cells. As a polymerization technique that initiates from the surface, electrodeposition improves the polymer filling rate inside ZnO nanostructures. We studied the interface between the e-PT film and ZnO (both planar and nanorod substrates) by XPS. We found that the e-PT film morphology can be tuned by the choice of solvent. Electrodeposition of conjugated polymers is generally applicable to other monomers and substrates.

17) TPD and DFT Studies of Adsorption and Desorption of H$_2$ on Planar and Faceted Ir(210)
Wenhua Chen$^1$, Payam Kaghazchi$^2$, Timo Jacob$^2$ and Robert A. Bartynski$^1$
$^1$Department of Physics and Astronomy, and Laboratory for Surface Modification and $^2$Institut für Elektrochemie, Universität Ulm, Germany

We report adsorption and desorption of H$_2$ on planar Ir(210) and faceted Ir(210) with tunable sizes of three-sided nanopyramids exposing (311), (31-1) and (110) faces using TPD and DFT. H$_2$ adsorbs dissociatively on Ir upon adsorption at 300K. At saturation coverage, two TPD peaks of H$_2$ appear at 360K and 440K from faceted Ir(210) while one peak is observed from planar Ir(210), indicating strong structure sensitivity in recombination and desorption of H$_2$. At fractional coverage, only one peak is seen at 440K on faceted Ir(210). No evidence has been found for size effects in desorption of H$_2$ from faceted Ir(210). Using DFT, we have determined energetically favorable binding sites and binding energies for H on Ir(210), Ir(311) and Ir(110), and generated surface phase diagrams under UHV conditions from which we can estimate H$_2$ desorption temperatures. The calculated behavior in desorption energies of H$_2$ from Ir is consistent with experimentally observed trends in desorption temperatures.

18) Reduction of NO by C$_2$H$_2$ on Planar and Faceted Ir(210)
Wenhua Chen, Quan tong Shen and Robert A. Bartynski
Department of Physics and Astronomy, and Laboratory for Surface Modification

Upon adsorption, C$_2$H$_2$ dissociates to form CCH and H species on the Ir surfaces at low C$_2$H$_2$ coverage. For adsorption of NO on C$_2$H$_2$-covered Ir, TPD data show that both surfaces exhibit high reactivity for reduction of NO with high selectivity to N$_2$ at low C$_2$H$_2$ pre-coverage, although the reaction is completely inhibited at high C$_2$H$_2$ pre-coverage. Co-adsorbed C$_2$H$_2$ significantly influences NO dissociation. The N-, H- and C-containing products are dominated by N$_2$, H$_2$ CO and CO$_2$ together with small amounts of H$_2$O. For adsorption of NO on C-covered Ir(210) at fractional C pre-coverage, formation of CO$_2$ is promoted while production of CO is reduced. Reduction of NO by C$_2$H$_2$ is structure sensitive on faceted Ir(210) versus planar Ir(210) but no evidence is found for size effects in reduction of NO by C$_2$H$_2$ on faceted Ir(210) for average facet sizes of 5-14nm. The results are compared to reduction of NO by CO on the same Ir surfaces.

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19) Study of Interfacial Nitrogen at the 4H-SiC/\text{SiO}_2 and Si/\text{SiO}_2 Interface
Yi Xu*,1,2, Gang Liu3, Hang Dong Lee4, Blair R. Tuttle5, Sokrates T. Pantelides5, John Williams6, Sarit Dhar6, Torgny Gustafsson4, Eric Garfunkel1,2 and Leonard C. Feldman1,2
1Department of Chemistry and Chemical Biology, 2Institute for Advanced Materials, Devices and Nanotechnology, 3Department of Electrical and Computer Engineering, 4Department of Physics and Astronomy, and Laboratory for Surface Modification, 5Department of Physics, Auburn University and 6Department of Physics and Astronomy, Vanderbilt University

SiC is a promising semiconductor for in many high temperature and high power applications, but is limited by the nature of dielectric/semiconductor interface. Introducing nitrogen at the interface shows significant improvement in electrical performance. In this work, X-ray photoelectron spectroscopy (XPS) is used to study the chemical states, interfacial structure and etching behavior of interfacial nitrogen. The experimental result and proposed models are also supported by the theoretical calculations. Quantification of nitrogen and phosphorus are investigated by XPS, ion scattering and secondary ion mass spectroscopy.

20) Development of Inorganic-Organic Crystalline Hybrid Materials for Energy Related Applications
Xiao Zhang*, Mojgan Roushan, Haohan Wu, Zhijuan Zhang, Jingming Zhang, Sanhita Pramanik and Jing Li
Department of Chemistry

Hybrid materials that incorporate organic and inorganic components into a single crystal lattice often lead to modified and enhanced properties, as well as new phenomenon and new functionality. Recently we have developed several classes of hybrid materials including inorganic-organic hybrid semiconductors and metal organic frameworks. The inorganic organic hybrid semiconductors comprising of sub-nanometer sized semiconductor motifs and organic diamines possess improved physical properties over their parent bulk materials. The metal organic frameworks built on metal ions linked by organic ligands demonstrate porosity associated multi-fold functionality that show great promise for applications in gas storage and separation, catalysis and sensing.
Molecular Design and Dipole Effects at Semiconductor

Alberto Batarseh*, Keyur Chitre, Andrew Kopecky, Elena Galoppini, Sylvie Rangan and Robert A. Bartynski

Chemistry Department, Rutgers University, Newark and Department of Physics and Astronomy, and Laboratory for Surface Modification

Organic-inorganic and organic-organic hybrid materials are used in a wide variety of application areas including molecular electronics and photovoltaics. This poster will illustrate our most recent work to tune at the molecular level energy level alignment, charge donation and withdrawal, and molecule bonding geometries of organic/semiconductor interfaces by using Head-Linker-Anchor (HLA) compounds with a built-in tunable dipole. The poster will describe the synthesis of HLA porphyrins PD2a and PD2b, where the linker unit contains a molecular dipole, obtained by introducing a donor and acceptor group on the Linker unit. The rigid linkers are designed to bind at a well-defined orientation and distance from the surface of organic crystal and inorganic semiconductors. The poster will focus on the synthesis and spectral characterization of the model compounds. Preliminary studies of the resulting organic/semiconductor interfaces through a combination of surface science techniques will be illustrated.

* = Student Presenter
22) **Scanning Tunneling Microscopy Observations of Zinc Tetraphenylporphyrin Molecules on Au(111) Surface: Packing Geometry and Substrate Interactions**

Charles Ruggieri*, Sylvie Rangan and Robert A. Bartynski  
*Department of Physics and Astronomy, and Laboratory for Surface Modification*

Scanning tunneling microscopy data of zinc tetraphenylporphyrin (ZnTPP) molecules on Au(111) are presented for monolayer and sub-monolayer coverages. Molecular packing order and modification of herringbone reconstruction as a function of molecular coverage and preparation conditions is discussed. In addition, a previously unreported substrate surface structure in the presence of molecules is observed.

23) **Binding Affinities of Iodine to Ruthenium Dyes**

Hao Tang*, Andrew Kopecky and Elena Galoppini  
*Department of Chemistry, Rutgers University, Newark*

Two ruthenium bipyridyl rigid rod compounds were employed to determine the binding affinities of iodine to ruthenium dyes. The binding affinities of iodine to ruthenium dyes in acetonitrile are in the range of 15000 – 30000 M$^{-1}$ while those on dye sensitized TiO$_2$ films are in the range of 3000 – 9000 M$^{-1}$. Results show that the alkyl chain in the dye molecule enhances the binding affinities of iodine to ruthenium dyes.

24) **Ultrafast Proton Coupled Electron Transfer (PCET) in UVA and UVB Absorbers**

Donald Prettypaul*, Jianhua Bao and Piotr Piotrowiak  
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The excited state dynamics of bis-ethylhexyloxyphenol methoxyphenyl triazine (Escalol$^\text{CS}$) which is a widely used UVB/UVA absorber, was studied using femtosecond pump-probe transient absorption spectroscopy. The compound exhibits very fast internal conversion and a short excited lifetime (a few picoseconds) with a strong response to solvent polarity, viscosity and the protic/aprotic nature. Furthermore, the excited state dynamics exhibits a strong H/D isotope effect pointing to the importance of the intramolecular proton coupled electron transfer (PCET) between the OH group of the phenol and the central triazine ring in the rapid deactivation of the excited state. The second investigated UVA absorber, butyl methoxydibezoylmethane (Escalol$^\text{517}$) exists as a mixture of ketone and two enol tautomers, each with a distinct ground state absorption and excited state dynamics. The equilibrium between the tautomers depends on the polarity and the protic/aprotic nature of the solvent as well. The enol forms are stabilized by an intramolecular hydrogen bond which plays an important role in the excited state dynamics.

* = Student Presenter
Excitons and Excess Electrons in Nanometer Size Polyoxotitanate Clusters: Electronic Spectra, Exciton Dynamics and Surface States
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The behavior of excitons and excess electrons in the confined space of a polyoxotitanate cluster \( \text{Ti}_{17} (\mu_4\text{O})_4 (\mu_3\text{O})_{16} (\mu_2\text{O})_4 (\text{OPr})_{20} \) (in short \( \text{Ti}_{17} \)) was studied using femtosecond pump-probe transient absorption, pulse radiolysis and fluorescence spectroscopy. Due to pronounced quantum size effects the electronic spectra of the exciton, \( \text{Ti}_{17}^* \), and the excess electron in the radical anion \( \text{Ti}_{17}^- \), are blue-shifted in comparison with bulk TiO\(_2\) and have maxima at 1.91 and 1.24 eV. The 0.7 eV difference in the position of the maxima \( \text{Ti}_{17}^* \) and \( \text{Ti}_{17}^- \) indicates the presence of strong Coulomb interaction between the conduction band electron and the valence band hole in the \( \sim 1 \) nm diameter cluster. Ground state Raman spectra and the vibronic structure of the fluorescence spectrum point implicate the interfacial ligand modes in the localization of the relaxed exciton. Exciton recombination in \( \text{Ti}_{17} \) is faster than in anatase nanoparticles. The kinetics exhibits three components, ranging from less than 1ps to 100 ps, which are tentatively assigned to the geminate recombination within the core of the cluster and to the decay of the surface stabilized charge transfer exciton. A persistent long-lived component with \( t > 300 \) ps may indicate the involvement of intraband dark states, i.e. triplet excitons \( \text{Ti}_{17}^* \).
Functionalization of Nanostructured ZnO Films by Copper-Free Click Reaction

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The poster will describe a novel surface functionalization methodology for ZnO nanorod films grown by metal organic chemical vapor deposition (MOCVD) involving copper-free click reaction. 11-Azidodecanoic acid was bound to ZnO nanorod films through the carboxylic acid moiety, leaving the azide group available for Cu-free click reaction with alkynes. The azide-functionalized layer was reacted with 1-ethynylpyrene, a fluorescent probe, and with alkynated biotin, a small biomolecule. The immobilization of pyrene on the surface was probed by fluorescence spectroscopy, and the immobilization of biotin was confirmed by binding with streptavidin-fluorescein isothiocyanate (streptavidin-FITC). The functionalized ZnO films were characterized by infra-red attenuated total reflectance (FTIR-ATR), steady-state fluorescence emission, fluorescence microscopy, and field emission scanning electron microscopy (FESEM). The application of this method to biosensor development will be discussed.

* = Student Presenter
27) Molecular Mechanisms of the Conversion Reaction in FeF$_2$ Cathodes Exposed to Li in High Capacity Batteries
Ying Ma and Stephen H. Garofalini
Interfacial Molecular Science Laboratory, Department of Materials Science and Engineering

Conversion materials such as iron fluorides enable access to the multiple valence states of the cathode cation, from the ionic to metallic state, in high capacity Li-ion batteries. To determine the detailed mechanisms and reaction pathways, we have developed a dynamically adaptive variable charge potential for MD simulations that describes behavior that was subsequently corroborated in experiments.

28) Topological Phase Transitions in In- and Sb-doped Bi$_2$Se$_3$
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Department of Physics and Astronomy, and Laboratory for Surface Modification

We use first-principles calculations to study the phase transition from a topological to a normal insulator in In- and Sb-doped Bi$_2$Se$_3$. The intrinsic spin-orbit coupling (SOC) strength is similar in In and Sb, which have similar atomic numbers, so if the topological transitions in the two doped systems are purely driven by the decrease of SOC strength, we would expect to see similar critical concentrations $x_c$ in (Bi$_{1-x}$In$_x$)$_2$Se$_3$ and (Bi$_{1-x}$Sb$_x$)$_2$Se$_3$. However, based on our calculations, the critical In concentration $x_c$ is expected to be between 6.25% and 12.5%, which is much lower than that of the Sb-doped case. In the latter case, the Sb $x_c$ is even above 87.5% based on supercell calculations, and around 65% based on the virtual crystal approximation (assuming no change of crystal structure).

To explain the difference, we find that the phase transition is mostly dominated by the decrease of SOC in the Sb-doped case. However, for In-doped Bi$_2$Se$_3$, the In 5s orbitals strongly suppress the topological band inversion at low concentrations, hence accelerating the occurrence of the phase transition. We also find a tendency of In atoms to segregate in the In-doped system.