TWENTY-EIGHTH ANNUAL SYMPOSIUM

of the

LABORATORY FOR SURFACE MODIFICATION

Friday, March 28, 2014

9:00 a.m. to 4:00 p.m.

Rutgers, the State University of New Jersey

PROGRAM

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

8:30  Registration, coffee
9:00  Introductory Remarks

Torgny Gustafsson  
Interim Director, Laboratory for Surface Modification

Leonard C Feldman  
Director, Institute for Advanced Materials, Devices and Nanotechnology

SESSION I:  
NEW VISTAS IN ELECTRON MICROSCOPY

Chair: Prof. Phil Batson  
Institute for Advanced Materials, Devices and Nanotechnology

9:15 – 10:00  What Could the New NION UltraSTEM Mean for Rutgers and the Scientific Community?  
Professor John Silcox  
Applied and Engineering Physics, Cornell University

In congratulating Rutgers University on the arrival of the new NION electron microscope, I will give some perspective on how this came to exist, discuss some background physics and chemistry and attempt to project albeit at a somewhat elementary level the kind of new science that might be expected to emerge, recognizing that it is likely to be the unforeseen discoveries that will be the most valuable results. Some comments on what will be required to achieve these desired results will be included.

10:00 – 10:30 Coffee Break and Poster Session

* = Student Presenter
Electron-optical instrumentation and applications have progressed greatly in the last few years. Nion company and Nion users have spearheaded several of the key developments. For instance, we introduced an ultra-stable scanning transmission electron microscope [1] that’s giving <1 nm per hour sample and defocus drift, and which has an ultra-bright, extreme-vacuum cold field emission electron gun [2]. We have also developed a monochromator that is now approaching 10 meV energy resolution [3].

The new instrument has led to several pioneering advances, such as acquiring atomic resolution electron energy loss spectroscopy (EELS) elemental maps (in 2008), performing EELS and energy-dispersive X-ray spectroscopy (EDXS) analysis on single atoms, performing fine-structure EELS analysis on single atoms, and more recently, acquiring EELS spectra at 12 meV energy resolution (Figure 1).

These developments will be described, together with our current projects such as developing open-source, Python-based data acquisition and processing software.


Fig. 1. Zero loss peak (ZLP) acquired with the Nion High Energy Resolution Monochromated EELS STEM (HERMES™) system. 60 keV, 0.25 s acquisition time.

11:15 – 11:30 Informal Remarks on the Intersection of Proteomics and Microscopy
Professor Stephen K. Burley
Director, Center for Integrative Proteomics Research, Rutgers University
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11:30-11:45  Attosecond and Femtosecond Forces Acting on Gold Nano-sized Particles Induced by Relativistic Electrons
Dr. Maureen Lagos
Institute for Advanced Materials, Devices and Nanotechnology, Rutgers University

When a relativistic electron passes a nanometer-sized metal particle (NP), it imposes electromagnetic (EM) forces that can both push and pull the particle. Although EM theory is well developed, a detailed understanding of the behavior of these forces still remains unclear. Here, we show results for calculations of the time-varying EM forces acting in a spherical gold NP, imposed by the passing electron. We find that the acting forces are generated at different stages of the EM interaction and their physical origins rely on different fundamental mechanisms. During the first stages of the process, the NP is subjected to attosecond impulse forces, which are generated by the moving external fields acting on the atomic charges and currents within the particle. Those forces exhibit both attractive and repulsive behavior which are mainly driven by the total electric and magnetic fields, respectively. Furthermore, femtosecond oscillatory reaction forces are generated in the subsequent stages of the process. These oscillatory forces are enabled by the well-known surface plasmon oscillations in the NP, triggered by the external excitation. They can be visualized as back recoil on charge density fluctuations due to likely emission of radiation.

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☕ 11:45 – 1:30 Lunch, Poster Session, and Tours of the new Electron Microscopy Facility ☕

ABSTRACTS OF THE POSTER PAPERS CAN BE FOUND ON PP. 9
SESSION II:

HELIUM MICROSCOPY – PRINCIPLES AND APPLICATIONS

Chair: Prof. Torgny Gustafsson
Department of Physics and Astronomy

1:30 – 2:15   A Cartoon Guide to the Helium Ion Microscope
Dr. John Notte
Director R&D, Carl Zeiss Microscopy LLC

From top to bottom, technology of this new instrument is broken down and explained for the curious minded. First and foremost, we cover the world’s brightest ion source, the heart of the instrument, where ions are repeatedly created within an atom-sized volume. We work our way down to the sample/target, where the helium ions impinge at a rate of 6 million per second. Finally, we cover the new uses for this instrument from imaging with sub-nanometer resolution, to nano-scale analysis, and even to nano-fabrication. Example applications will be cited from diverse fields of biology, polymer science, semiconductor devices, materials science, and chemistry.

2:15 – 2:45   Finding and Characterizing Metal Nanoparticulates in Biological Tissues
Dr. J. Albert Schultz
President, Ionwerks INC

Helium Ion microscopy begins to build a home in biology. One room in this outdwelling will involve molecular Imaging of tissues by implantation of 6nm AgNP (also Au, Pt, Al) which then enables a remarkably reproducible molecular surface analysis by MILDI-MSI (Matrix Implantation Laser Desorption/Ionization Mass Spec imaging). The need of our collaboration (Rutgers, Ionwerks, Carl Zeiss, and the National Institute on Drug Abuse (NIH-NIDA and Ionwerks)) to measure the precise number of Ag atoms and nanoparticles in the near surface of a tissue can be ideally fulfilled by backscattering and recoil analysis and SIMS (Secondary Ion MS) within the Zeiss Orion. The hardware—present and future—to perform these experiments will be briefly described.

Partial support through NIH Phase II NIH SBIR grants 5R44DA030853-04 and 2R44DA036263-02 to Ionwerks is gratefully acknowledged.
2:45 – 3:00  Ion Beam and Helium Microscopy Study of Brain Tissue Implanted with Ag Nanoparticles for MALDI Applications
Dr. Samir Shubeita¹, Hang Dong Lee², Can Xu², Damon Barbacci³, Katrin Baldwin³, Ludovic Muller³ Amina Woods³, Albert Schultz⁴, Leszek Wielunski², Torgny Gustafsson² and Leonard C. Feldman¹
¹Institute for Advanced Materials, Devices and Nanotechnology, ²Department of Physics and Astronomy, ³NIDA-IRP, Baltimore, MD and ⁴Ionwerks Inc., Houston, TX

MALDI (Matrix Assisted Laser Desorption/Ionization) mass spectrometry of tissues implanted with Au and Ag nanoparticles gives a vastly enhanced desorption yield of biomolecules compared to unimplanted samples. To interpret and quantify this effect requires knowledge of the spatial distribution of the implanted nanoparticles. We use Rutherford Backscattering and Helium Ion Microscopy imaging to determine the Ag NP distributions in implanted rat brain tissues and correlate our results with those from the spatially defined MALDI intensity and biomolecular ion distribution. The results show good Ag distribution uniformity and increased MALDI intensity that is a non-monotonic function of the Ag implantation dose.

This work is partially supported by NSF (DMR 1126468), NIH, and IAMDN.
3:00 – 3:15 Move to the Nanophysics Laboratory Room 111

3:15 – 4:00 Presentation of Theodore E. Madey Student Awards for Best Poster Presentation

Tour of the Helium Ion Microscope

Refreshments, cheese and wine
ABSTRACTS FOR POSTERS

QUANTUM MATERIALS

1) Magnetic Field-Induced Toroidal Moment and Linear Magnetoelectricity in Fe-Langasite
Sergey Art'yukhin, David Vanderbilt and Sang-Wook Cheong

Department of Physics and Astronomy

Multiferroic and magnetoelectric materials are of pressing interest for applications in spintronics and information storage technology. Magnetic field control of inversion-breaking spin textures in frustrated magnets opens a way to magnetic control of polarization. Here we discuss a ferrotoroidal ordering, induced by magnetic field in Fe-langasite, and explain the peculiar magnetoelectric effect in this material.

2) Nematic Fluctuations Probed by Raman Scattering in EuFe2As2
Wei-Lu Zhang1,2,*, Verner Thorsmolle3, Hsiang-Hsi Kung1, Philip Lubik2, Alexander Lee2, Girsh Blumberg2, Pierre Richard1, Hong Ding1 and Athena S. Sefat3

1Chinese Academy of Sciences, 2Department of Physics and Astronomy, 3Oak Ridge National Lab

Raman scattering is a technique to study the phonon, charge carriers and spin excitations. Here we present a polarization resolved electronic Raman measurement of the iron pnictide parent compound EuFe2As2 from room temperature to 12 K. We observe a quasi-elastic peak (QEP) in B_{2g} symmetry channel reflecting the nematic fluctuations in the stress-free tetragonal phase. The QEP intensity is maximized at T_S/T_{SDW} and rapidly clears up in the low temperature orthorhombic phase. In the tetragonal phase, the scattering rate \Gamma shows linear temperature dependence. The Raman conductivity at zero energy \chi_0 follows a Curie Weiss law with a Weiss temperature of 83 K. A Fano shaped optical phonon mode is observed in the B_{2g} symmetry channel for below T_S/T_{SDW}.

3) Dynamical Magnetic Charges and Linear Magnetoelectricity
Meng Ye* and David Vanderbilt

Department of Physics and Astronomy

Magnetoelectric (ME) materials are of fundamental interest and are investigated for their broad potential applications. In several materials, the dominant contribution to the ME response has been shown to be the ionic term, which is proportional to both the Born charge Z_e and its analogue, the dynamical magnetic charge Z_m. Here we present a theoretical study of mechanisms that could enhance the magnetic charge Z_m. The KITPite structure is reported with large ME response arising from exchange striction and spin frustration. Using first-principles density-functional methods, we calculate the atomic Z_m tensors in KITPite and conclude that even when SOC is completely absent, the exchange striction acting on the non-collinear spin structure induces much larger magnetic charges than in the case when Z_m is driven by SOC as in Cr2O3.
4) Transfer of Large-Area MBE Grown Bi$_2$Se$_3$ Films to Arbitrary Substrates and Metal-Insulator Transition via Dirac Gap
Namrata Bansal$^1*$, Matthew Brahlek,$^2$ Nikesh Koirala,$^2$ Yoichi Horibe,$^2$ Jing Chen,$^2$ Weida Wu$^2$ and Seongshik Oh$^2$

$^1$Department of Electrical and Computer Engineering, $^2$Department of Physics and Astronomy

We present an alternative process to transfer the entire area, 1 cm $\times$ 1 cm lateral size, of topological insulator (TI) Bi$_2$Se$_3$ thin films, grown epitaxially on Al$_2$O$_3$ and SiO$_2$ to arbitrary substrates; resulting in films with lower carrier concentrations and higher mobilities than before the transfer. Atomic force microscopy and transmission electron microscopy further confirm the pristine morphology and crystallinity of the transferred films. Furthermore, utilizing this process, we show that as the Fermi level is tuned into the proximity gap at the Dirac point of an ultrathin film, the film makes a clear metal-insulator transition with more than four orders of resistance change.

5) Engineering Heterostructure of Topological Insulator and Trivial Insulator
Nikesh Koirala$^1*$, Matthew Brahlek$^1$, Jianpeng Liu$^1$, Maryam Salehi$^1$, Tahir Yusafaly$^1$, David Vanderbilt$^1$ and SeongShik Oh$^1$

$^1$Department of Physics and Astronomy and $^2$Department of Material science and Engineering

For the prototypical topological insulator (TI) Bi$_2$Se$_3$, band insulator (I) In$_2$Se$_3$ can be used to grow atomically sharp TI-I-TI heterostructure using molecular beam epitaxy due to their structural compatibility, which allows one to study evolution of topological surface states (TSS) at the interface between them. Weak Anti-localization measurements along with first principle calculation reveal the coupling process between top and bottom Bi$_2$Se$_3$ films as a function of In$_2$Se$_3$ barrier thickness. For In$_2$Se$_3$ thicker than $\sim$2-3nm, Bi$_2$Se$_3$ films are completely decoupled and gapless TSS emerge at the TI-I interface. By replacing In$_2$Se$_3$ with solid mixture (Bi$_x$In$_{1-x}$)$_2$Se$_3$, barrier transparency can be varied by varying x leading to further tunability of this coupling.

6) Topological Structural Vortices in Hexagonal Manganites and the Kibble-Zurek Mechanism
Xueyun Wang* and Sang-Wook Cheong
Rutgers Center for Emergent Materials

Hexagonal REMnO$_3$ (RE=Y, Ho-Lu) is an improper ferroelectric, in which a ferroelectric-trimerization structural phase transition induces topological structural vortices. We have carefully examined how the vortex density changes with the cooling rate across the transition temperature, as well as the scaling relationship between winding number and domain size. These results are compared with the prediction of the Kibble-Zurek mechanism, which is relevant to the topological defect formation though a non-equilibrium process in a continuous phase transition such as the formation of cosmic strings right after big bang.

* = Student Presenter
7) **Effective J=1/2 Insulating State in Ruddlesden-Popper Iridates: An LDA+DMFT Study**  
*Hongbin Zhang, Kristjan Haule and David Vanderbilt  
*Department of Physics and Astronomy*

The competition between spin-orbit coupling and electron correlations in 5d compounds gives rise to many interesting phenomena. One particularly attractive case is the effective J=1/2 insulating phase found in the first member of Ruddlesden-Popper (RP) iridates Sr$_2$IrO$_4$. Using *ab-initio* methods, we investigate the metal-insulator transition across the RP iridates and explore the robustness of the effective J=1/2 state against band effects due to itineracy, tetragonal distortion, octahedral rotation and Coulomb interaction. The electronic structures we obtained are in good agreement with recent ARPES measurements.

8) **Tuning the Kondo effect in graphene in the presence of point defects**  
*Jinhai Mao, Yuhang Jiang, Guohong Li, and Eva Y. Andrei  
*Department of Physics and Astronomy*

Removing a single carbon atom from the honeycomb lattice in graphene produces a localized state orthogonal to the undisturbed lattice states. According to theory this will give rise to a local magnetic moment when occupied by an electron, but its fate in the presence of conduction electrons is not known. Will it be screened by many body interactions below a critical Kondo temperature to form a singlet state, or will it remain unscreened? Recent studies using transport or magnetic measurements on graphene in the presence of point disorder have reached opposite conclusions. We addressed this question by combining STM and transport measurements to study the effect of interactions between the electrons in graphene and local magnetic moments as a function of carrier density and dielectric environment. At high density we observe a clear signature of Kondo screening in the form of a Fano resonance in the density of state that is pinned to the Fermi energy and splits in a magnetic field. We further find that the Kondo temperature strongly depends on the carrier density and that it can be tuned in or out with a gate voltage.

Supported by DOE-FG02-99ER45742 and NSF DMR 1207108

9) **Thermo-Optic Effect in Silicon Photonic Crystal Waveguide Electro-Optic Devices**

Wei Jiang\(^1,3\), Weiwei Song\(^1\)*, Jun Tan\(^1\)*, Manjit Chahal\(^1\)*, Siamak Abbaslou\(^1\)*, George K. Celler\(^2,3\) and Yogesh Jaluria\(^4\)

\(^1\)Department of Electrical and Computer Engineering, \(^2\)Department of Materials Science and Engineering, \(^3\)Institute for Advanced Materials, Devices, and Nanotechnology, \(^4\)Department of Mechanical and Aerospace Engineering

Silicon electro-optic (EO) devices can offer a wide range of functionalities such as optical modulation, switching and dynamic wavelength add-drop. In silicon electro-optic devices, thermo-optic (TO) effect often co-exists, and counter-acts the EO effect. This work quantifies the relative magnitude of the electro-optic effect versus thermo-optic effect in such devices.

10) **Helium Ion Microscopy and Medium Energy Ion Spectroscopy of a-face SiC Surface After Reactive Ion Etching**

Hang Dong Lee\(^1,2\), Samir M. Shubeita\(^1,2\), Can Xu\(^1,2\), Gang Liu\(^2\), Leonard Feldman\(^1,2\) and Torgny Gustafsson\(^1,2\)

\(^1\)Department of Physics and Astronomy, \(^2\)Institute for Advanced Materials, Devices and Nanotechnology

Reactive ion etching (RIE) is a process required in fabrication of SiC UMOSFET. However, RIE always results in serious damage and contamination of the SiC surface. Helium Ion Microscope (HIM) images of an a-face SiC surface after RIE showed severe structural damage and large scale morphological changes corroborated by Medium Energy Ion scattering spectroscopy (MEIS). HIM and MEIS also showed that etching in H\(_2\) at 1400 °C could remove the surface damage. C-V measurements demonstrated the electrical recovery of the surface after the etching. This work was supported by the National Science Foundation grant DMR-1106070, DMR-1126468 and ARL and II-VI Foundation.

11) **The Absorption of Water Vapors as a Probe to Study the Properties of Thermal Oxides on SiC and Si**

Gang Liu\(^1\), Boris Yakshinskiy\(^1\), Leszek Wielunski\(^1\), Can Xu\(^1\), Torgny Gustafsson\(^1\), Joseph Bloch\(^1,3\) and Leonard Feldman\(^1,2\)

\(^1\)Department of Physics and Astronomy, \(^2\)Institute for Advanced Materials, Devices and Nanotechnology, \(^3\)NRCN, Beer-Sheva, Israel

We combine Nuclear Reaction Analysis (NRA) and electrical (C-V and I-V) measurements to study thermal oxides grown on Silicon Carbide (SiC) and Si. We use D\(_2\)O, with ultra-sensitive detection as low as 1x10\(^{12}\)/cm\(^2\) to characterize both the semiconductor-oxide interface and the bulk oxide. Surprisingly, post-oxidation treatments (NO and Ar) have substantial effect on water absorption in oxidized SiC and almost no effect on Si oxidized under identical conditions.
Hydrogen Ion Implantation Assisted Exfoliation of SiC

Voshadhi P. Amarasinghe\textsuperscript{1,2,4,*}, Leszek Wielunski\textsuperscript{1,3}, A. Barcz\textsuperscript{5}, Leonard. C. Feldman\textsuperscript{1,2,3} and George K. Celler\textsuperscript{1,2}
\textsuperscript{1}Institute for Advanced Materials, Devices, and Nanotechnology (IAMDN), \textsuperscript{2}Department of Materials Science and Engineering, \textsuperscript{3}Department of Physics, \textsuperscript{4}Department of Chemistry and \textsuperscript{5}Institute of Electron Technology/Institute of Physics PAS, Warsaw, Poland

Hydrogen ion beam implantation assisted exfoliation of single crystalline silicon carbide (SiC) is used to study the influence of implantation temperature on SiC layer exfoliation. TRIM calculation, RBS, and SIMS data were used to identify the damage and concentration profiles caused by the hydrogen implantation. Hydrophilic bonding of two oxidized surfaces was used to transfer the exfoliated SiC layers. And post exfoliation layer quality was also explored in the study.

Structure and Composition of the 4H-SiC Surface and Dielectric Interface

Can Xu\textsuperscript{1,3,*}, Hang Dong Lee\textsuperscript{1,3}, Samir Shubeita\textsuperscript{1,3}, Gang Liu\textsuperscript{3}, Yi Xu\textsuperscript{2,3}, Leszek Wielunski\textsuperscript{1,3}, Eric Garfunkel\textsuperscript{2,3}, Torgny Gustafsson\textsuperscript{1,3} and Leonard C. Feldman\textsuperscript{1,3}
\textsuperscript{1}Department of Physics and Astronomy, \textsuperscript{2}Department of Chemistry and Chemical Biology, \textsuperscript{3}Institute for Advanced Materials, Devices and Nanotechnology

Atomic vibrations in solids represent a crystal “disorder” that needs to be included in the evaluation of many materials structural probes. To the extent that atomic bonding links these vibrations (correlated vibrations) this “disorder” is reduced. We have used Medium Energy Ion Scattering (MEIS) to study the role of surface vibrations on ion scattering of both the Si-face SiC (0001) and the C-face SiC (000-1). We report a very large correlation effect of the atomic vibrations at the SiC surface and discuss the need for correlations to be included more completely in theoretical descriptions in atomic collision-solid interactions.

This work was supported by the National Science Foundation grant DMR-1106070 and the U.S. Army Research Laboratory W911NF-07-2-0046 and the II-VI Foundation Block-Gift Program.

Thermo-Optic Effect in Silicon Photonic Crystal Waveguide Electro-Optic Devices

Robert Gatdula\textsuperscript{1,*}, Weiwei Song\textsuperscript{1}, Jun Tan\textsuperscript{1}, Manjit Chahal\textsuperscript{1}, Siamak Abbasi\textsuperscript{1}, George K. Celler\textsuperscript{2,3}, Yogesh Jaluria\textsuperscript{4} and Wei Jiang\textsuperscript{1,3}
\textsuperscript{1}Department of Electrical and Computer Engineering, \textsuperscript{2}Department of Materials Science and Engineering and \textsuperscript{3}Institute for Advanced Materials, Devices, and Nanotechnology, \textsuperscript{4}Department of Mechanical and Aerospace Engineering

Silicon electro-optic (EO) devices can offer a wide range of functionalities such as optical modulation, switching and dynamic wavelength add-drop. In silicon electro-optic devices, thermo-optic (TO) effect often co-exists, and counter-acts the EO effect. This work quantifies the relative magnitude of the electro-optic effect versus thermo-optic effect in such devices.

* = Student Presenter
15) **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$^4$, B. R. Tuttle$^5$, S. T. Pantelides$^5$, John Williams$^6$, Sarit Dhar$^6$, Torgny Gustafsson$^4$, Eric Garfunkel$^{1,2}$ and Leonard C. Feldman$^{2,6}$

$^1$Department of Chemistry and Chemical Biology, $^2$Instititue for Advanced Materials, Devices and Nanotechnology, $^3$Department of Electrical and Computer Engineering, $^4$Department of Physics and Astronomy, $^5$Department of Physics, Auburn University, $^6$Department of Physics and Astronomy, Vanderbilt University

SiC is a promising semiconductor for 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.

16) **High Sensitivity Deuterium Detection in Thin Films using Nuclear Reaction D($^3$He, p)$^4$He with 740 keV $^3$He Ion Beam**

Leszek Wielunski$^1$, Boris Yakshinskiy$^1$, Gang Liu$^2$, Can Xu$^1$, Torgny Gustafsson$^1$, Joseph Bloch$^{1,3}$ and Leonard Feldman$^{1,2}$

$^1$Department of Physics and Astronomy, $^2$Institute for Advanced Materials, Devices and Nanotechnology, $^3$NRCN, Beer-Sheva, Israel

The reaction D($^3$He, p)$^4$He is highly exothermal and most suitable for D determination in the near-surface region of solids. Here, we have performed Nuclear Reaction Analysis (NRA) of deuterium-containing oxidized SiC and SiO$_2$ samples using Tandem accelerator. We achieved sensitivity for deuterium detection of $\sim 2 \times 10^{12}$ D/cm$^2$ by using a set of 3 in-plane placed surface barrier solid state detectors. For deuterium concentration estimations the calibrated D-implanted Si wafer was utilized. The stainless steel foil was placed in front of the detectors to stop unwanted scattered particles.
The Mechanism of Catalytic Water Oxidation by Cobalt: From Cubanes to Materials
Paul F. Smith*, Christopher Kaplan, John E. Sheats, David M. Robinson, Nicholas S. McCool, Nicholas Mezle, and G. Charles Dismukes
Department of Chemistry and Chemical Biology

The oxidation of water to molecular oxygen is a thermodynamically difficult 4-electron, 4-proton process which must precede hydrogen production. It requires a catalyst capable of obtaining multiple intermediates which are frequently unstable and thus complicate mechanistic studies. In this work, we report the most recent findings regarding mechanism of water oxidation as catalyzed by: 1) the biomimetic $\text{Co}_4\text{O}_4$ “cubane”, 2) crystalline heterogeneous cobalt catalysts $\text{Co}_3\text{O}_4$ and $\text{LiCoO}_2$, 3) homogeneous cobalt clusters of nuclearity less than four, and 4) relation to amorphous cobalt oxides. We describe how the $\text{Co}_4\text{O}_4$ cubane is an efficient metal-oxo motif when designing water oxidation catalysts.

Site Occupation and Strain in Transition Metal Dichalcogenides
Keivan Esfarjani$^{1,2}$, Manish Chhowalla$^{1,3}$ and Tewodros Asefa$^{1,4}$

$^1$Institute for Advanced Materials, Devices and Nanotechnology, $^2$Department of Mechanical Engineering, $^3$Department of Materials Science and Engineering, $^4$Department of Chemistry and Chemical Biology

Our recent work on MoS$_2$ and other transition metal dichalcogenides (TMDC) has shown that these materials can behave as good catalysts for hydrogen evolution. Having a cheap alternative to Pt for this reaction makes these materials very attractive for such applications. While the strained metastable 1T phase shows a high catalytic activity, the more stable 2H phase does not. In order to investigate the thermodynamics and the strain state of this material at a given temperature, we construct a lattice gas model to describe the most stable 2H and 1T phases. The parameters of this model can be extracted for any TMDC system considered, by fitting to total energies calculated from first-principles. More generally, however, Monte Carlo simulations allow us to deduce a phase diagram for this coarse grained model. This implies that the phase and domain structure, if any, can be calculated at any temperature and for any value of the model Hamiltonian parameters. In this work we investigate the effect of the Hamiltonian parameters, vacancy concentration and temperature on the domain structure and the resulting strain state in the material.

* = Student Presenter
19) **Water-Splitting Electrocatalysts: A Comparison of Earth Abundant Materials and the Noble-Metal Standard**

Graeme Gardner*, Clyde Cady, Yong Bok Go, Martha Greenblatt and G. Charles Dismukes

*Department of Chemistry and Chemical Biology*

We examine the catalytic performance of a select group of well-characterized, crystalline materials that have previously reported high activities toward the oxygen evolution reaction (OER), one half-reaction of the overall water-splitting process. The earth-abundant metal-based catalysts are inspired by the core of the water-splitting enzyme in photosynthesis, PSII. They are bixbyite α-Mn$_2$O$_3$, and cubic lithium cobalt oxide, LiCoO$_2$. We compare them to a highly active, commercial standard iridium catalyst. Catalytic activity and stability are measured in a configuration that normalizes for active area, and electronic conductivity differences, such that no bias is present and the intrinsic activity of the crystalline polymorph is assessed.

20) **Ni$_5$P$_4$ a Game Changing H$_2$ Evolution Catalyst**

Anders B. Laursen$^{1}$, Kelly R. Patraju$^{1}$, Mariana J. Whitaker$^{1}$, Tapati Sarkar$^{2}$, Nan Yao$^{3}$, Kandalam V. Ramanujachary$^{4}$, Martha Greenblatt$^{1}$ and G. Charles Dismukes$^{1}$

$^{1}$*Department of Chemistry and Chemical Biology, $^{2}$Uppsala University, Sweden, $^{3}$PRISM Imaging and Analysis Center Princeton University, $^{4}$Department of Chemistry, Rowan University*

Hydrogen produced from fossil-free resources, *e.g.* electrocatalytic water-splitting, could not only introduce “the hydrogen economy” but is also an industrially relevant bulk chemical with a current ~10$^8$ ton annual production from natural gas. In electrochemical water-splitting platinum and nickel (or alloys thereof) are the electrocatalysts of choice for the hydrogen evolution reaction (HER) in acid and alkali, respectively. The scarcity of platinum, and the low efficiency of nickel, have greatly restricted the development of renewable hydrogen. Molecular nickel organophosphine complexes and recently the crystalline solid Ni$_2$P have proven highly active HER catalysts but both decompose during operation. Here we report, that the Ni$_5$P$_4$, outperforms Ni$_2$P and is comparable to platinum in its electrical efficiency for HER (kinetics and intrinsic overpotential). Unlike for Ni$_2$P, Ni$_5$P$_4$ is corrosion resistant in both strong acid and alkali during electrocatalysis. We will present a structural basis for the unusually high catalytic activity and corrosion resistance.
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BIOLOGICAL AND MEDICAL APPLICATIONS

21) Nanotechnology-Based Approaches to Control Stem Cell Neuro-Differentiation
Shreyas Shah*, Sahishnu Patel, Aniruddh Solanki, Perry Yin, Dean Chueng and Ki-Bum Lee
Department of Chemistry & Chemical Biology

Damage to the central nervous system is particularly devastating due to its limited regenerative capabilities. Among current methodologies, stem cell-based regenerative medicine shows great promise for achieving functional recovery. However, controlling stem cell fate and understanding the signaling pathways involved is one of the most important issues to address in order to harness the full potential of stem cells for regenerative therapies. To this end, we have successfully employed nanotechnology-based approaches, including the development of novel biomolecule nanocarriers and nanomaterial-based hybrid surfaces, to control the differentiation of stem cells into specific neural lineages (e.g. neurons, oligodendrocytes).

22) Graphene-Nanoparticle Hybrid Biosensors to Enhance the Detection of Disease Biomarkers
Perry T. Yin¹*, Sung Myung² and Ki-Bum Lee¹,²
¹Department of Biomedical Engineering, ²Department of Chemistry and Chemical Biology

Graphene is a single-atom thick, two-dimensional sheet of carbon that is characterized by exceptional chemical, electrical, material, optical, and physical properties. As a result, graphene and related materials, such as graphene oxide and reduced graphene oxide, have been brought to the forefront in the field of sensing. Recently, a number of reports from our lab and others have demonstrated that graphene-nanoparticle hybrid structures can act synergistically to offer a number of unique physicochemical properties that are desirable and advantageous for various sensing applications. These graphene-nanoparticle hybrid structures are particularly interesting because not only do they display the individual properties of the nanoparticles and of graphene, but they can also exhibit additional synergistic properties thereby enhancing the achievable sensitivity and selectivity using a variety of sensing mechanisms. Herein we demonstrate novel graphene-nanoparticle hybrid biosensors for the diagnosis of cancer as well as pancreatitis.

23) Multifunctional Nanomaterials for Cancer and Stem Cell Therapy and Imaging
Nicholas Pasquale¹*, Birju Shah¹, Prasad Subramaniam¹, Jinping Lai¹, Cheoljin Kim¹, Joung Kyu Park¹ and Jongjing Jung¹
Chemistry and Chemical Biology

In these presented works, magnetic nanoparticles, mesoporous silica nanoparticles, quantum dots and cyclodextrin-conjugated dendrimers are all used for advanced drug delivery applications. Our non-toxic multi-functional nanoparticles allow for the delivery of therapeutics, while simultaneously imaging their delivery. These materials show great promise as theranostic agents.

* = Student Presenter
Characterization of LiFePO$_4$ Cathode Nanocrystals by HRTEM and STEM/EELS Analysis

J. Schneider-Haefner$^1$, D. Tran$^1$, Y. Wang$^2$, J. Fang$^2$, N. Chernova$^2$ and F. Cosandey$^1$

$^1$Department of Materials Science and Engineering and $^2$Materials Science Department, Binghamton University

LiFePO$_4$ is currently in use as cathode material for rechargeable Li-Ion batteries because of its safety, low cost and high charge-discharge rate capabilities. In this study we have investigated the structure and morphology of LiFePO$_4$ nanocrystals produced by a simple chemical solution processing method. Nanocrystals ranging in size from 20 to 80 nm were produced and characterized by HRTEM and STEM/EELS analysis. The overall battery capacity has been optimized via a range in synthesis chemistry and annealing conditions. Variations in the Fe valence state were observed after various stages of delithiation process using Electron Energy Loss Spectroscopy (EELS).

Studies of the Synthesis and Deposition of Cu$_3$BiS$_3$ for use in Photovoltaic Devices

Joshua A. Epstein$^*$ and Dunbar P. Birnie III

Materials Science and Engineering

We are working with an earth abundant semiconductor material, copper bismuth sulfide, for use in thin film photovoltaic devices. We have developed an environmentally friendly, low temperature chemical pathway to synthesize CBS. We will be presenting our studies of the growth morphology of CBS coatings made using a benchtop reactor.

Zinc Tetraphenylporphyrins on Au(111): Adsorption Geometry and Energy Alignment at the Interface

Charles Ruggieri$^*$, Sylvie Rangan and Robert A. Bartynski

Department of Physics and Astronomy

The interaction between Zinc Tetraphenylporphyrin (ZnTPP) molecules and a Au(111) surface, from initial adsorption sites to monolayer organization, is investigated using scanning tunnel microscopy with a particular emphasis on registry of the overlayer and surface atomic structure. Additionally, electronic energy level alignment studies using photoemission and inverse photoemission spectroscopies are presented.

Examination of Microstructural Liquid Phase Behavior during Heat Treatment of Doped – PbTe Thermoelectric Materials

Sean Langan$^*$ and Dunbar P. Birnie III

Materials Science and Engineering

Thermoelectric materials offer a potentially valuable source of energy by converting a temperature gradient to electricity, but are limited by low efficiency and difficult production routes. Liquid phase sintering was attempted on lead telluride in an effort to shorten sintering time and produce favorable microstructures. These results are reported here.
28) Characterization of the Li-CoO Reaction with ARXPS  
Ryan Thorpe*, Sylvie Rangan, and Robert A. Bartynski  
Department of Physics and Astronomy

CoO nanoparticles have exhibited promising electrochemical properties when used as electrode materials in Li-ion conversion batteries. In order to characterize the Li-CoO reaction, thin films of CoO have been grown in three different orientations and exposed to Li in ultra-high vacuum. ARXPS was used to obtain depth-resolved information about the phase progression of these films as a function of Li exposure. Differences in reactivity and the uniformity of the reaction front were observed between the different oriented films.

29) Structural Transformations of FeOF/C Nanocomposite Electrode Upon Cycling In Li-ion Batteries  
Mahsa Sina¹, N. Pereira¹,², G. G. Amatucci¹,² and F. Cosandey¹  
¹Department of Materials Science and Engineering, ²Energy Storage Research Group

Iron oxyfluoride-carbon (FeOF/C) nanocomposites have been considered as alternative high energy density cathode materials since they have a theoretical capacity in excess of 700 mAhg⁻¹. In this study, the structural changes of FeOF/C positive electrode during lithiation/delithiation have been studied as a function of number of cycles under constant cycling current of 50 mA/g and at 60°C. ADF-STEM imaging technique combined with electron energy loss spectroscopy (EELS) and selected area electron diffraction (SAED) techniques were used to track the phase evolution of FeOF/C and chemical composition with bonding characteristics of phases present after cycling. Simulations of SAED patterns for nanoparticles in the 2-4 nm range were obtained ab-initio using JEMS program. The results of this investigation show that the amount of SEI layer (side reactions between the electrode and the electrolyte) increased with the number of cycles, which led to the loss of active materials and therefore incomplete reconversion reactions.

30) Energy Level Alignment of Polythiophene/ZnO Hybrid Solar Cells  
Wenchun Feng¹*, Sylvie Rangan², Yan Cao³, Elena Galoppini³, Robert A. Bartynski² and Eric Garfunkel¹,²  
¹Department of Chemistry and Chemical Biology, ²Department of Physics and Astronomy, ³Department of Chemistry

Energy level alignment at interfaces is critical for organic photovoltaics (OPV) as band offsets of the donor and acceptor materials largely determine the open circuit voltage (Voc) of the device. Using ultraviolet and inverse photoemission spectroscopy (UPS/IPS), we examined the correlation between energy level alignment and photovoltaic properties of a model bilayer hybrid solar cell incorporating electrodeposited polythiophene (e-PT) films on ZnO. The electrolyte anion (BF₄⁻, PF₆⁻, ClO₄⁻ or CF₃SO₃⁻) in the electrodeposition solution was found to have strong influence on e-PT film morphology and adhesion, energy level alignment at the interface, and ultimately the Voc of the photovoltaic devices.

* = Student Presenter
31) **Nitrogen- and Oxygen-Induced Faceting of Re(11\(\bar{1}\)1)**  
Hao Wang, Wenhua Chen and Robert A. Bartynski  
*Department of Physics & Astronomy*

The nitrogen- and oxygen-induced faceting of Re(11\(\bar{1}\)1) have been studied in detail by LEED and STM. At low nitrogen coverage, the Re(11\(\bar{1}\)1) surface shows a (2\(\times\)1) reconstruction, which acts as a precursor state for two-sided ridges formed at high coverage. Oxygen adsorption leads to a coverage-dependent morphological evolution, ranging from saw-tooth chains, 3-sided pyramids to four-sided pyramids. We have found microscopic structural connections between these various morphologies on the faceted Re(11\(\bar{1}\)1) surfaces, which provide a natural explanation for the mass transport pathways in the structural evolution.

32) **Wetting and Growth of Ionic Liquid Thin Films**  
Aleksandra B. Biedron*, Edward W. Castner, Jr. and Eric L. Garfunkel  
*Dept. of Chemistry and Chemical Biology and Nanotechnology for Clean Energy IGERT*

Surface studies of ionic liquids like 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide are possible thanks to their negligible vapor pressure. The complex interactions that occur between ILs and solids and at the IL-vacuum interface can lead to an array of ionic organization and wetting behavior. Understanding ion ordering at a solid interface could lead to optimized electrolyte-electrode interfaces in energy storage devices. Ultrathin films of ranging from monolayer to several tens of nanometers in thickness were prepared using physical vapor deposition and spin coating. The films were analyzed with complementary methods including X-ray photoelectron spectroscopy and atomic force microscopy.

33) **Elastic and Inelastic Helium Atom Scattering from L-alanine Structures on Cu(001)**  
Erkan Z. Ciftlikli and B. Jane Hinch  
*Department of Chemistry and Chemical Biology*

Dissociative L-Alanine adsorption on Cu(001) produces up to 4 domains of a c(4x2) superstructure at 0.5ML and below, which are stable under He beams and at up to ~200°C. Experimentally, at least one of 4 domains is virtually absent as a diffraction peak intensity is seen to almost disappear at certain He-beam energies. Unequal probabilities of 4 domains, then gives a clear indication of chirality within each domain’s diffraction, reflecting the innate chirality of the adsorbate. 2D angle-resolved HAS also shows low intensity streaks of highly inelastic intensity, which result from helium atom coupling into bound state resonances above Ala/Cu(001). The enhanced inelastic scattering intensities display a nearly dispersionless 5meV methyl rocking mode. Sub-saturation L-Ala/Cu(001) surfaces prepared and measured at higher sample temperatures were employed to measure the vibrational modes of isolated alaninate species.

* = Student Presenter

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34) **Fabrication of homogeneous metal nanopatterned surface using laser interference lithography technique**

Tae-Hyung Kim¹, Cheol-Heon Yea¹ and KiBum Lee¹,²

¹Department of Chemistry and Chemical Biology and ²Department of Biomedical Engineering

The fabrication of homogeneous metal nanopatterned surface has been a great of interest due to its high surface-to-volume ratio, reliability and reproducibility. Here, we report a method to generate extremely homogeneous metal nanostructures on the transparent electrode surface via laser interference lithography (LIL) combined with E-beam deposition and electrochemical reduction methods. Nanostructures with different sizes, shapes and heights were successfully generated on ITO electrode surface that were confirmed by scanning electron microscopy (SEM). Our new technology will be very useful for various kinds of applications including but not limited to energy storage devices or optical/electrical/electrochemical biosensors.

35) **Mapping High Explosives in the Vapor-phase with Luminescent Metal-Organic Frameworks**

Zhichao Hu*,¹ Sanhita Pramanik,¹ Kui Tan,² Chong Zheng,¹ Wei Liu,¹ Xiao Zhang,¹ Yves J. Chabal² and Jing Li¹

¹ Department of Chemistry and Chemical Biology, ² Department of Material Science and Engineering, University of Texas-Dallas, ³ Department of Chemistry and Biochemistry, Northern Illinois University

The effective detection of chemical explosives plays a crucial role in anti-terrorism applications. In optical sensing, it is challenging to differentiate explosive molecules of similar electronic properties since they often lead to similar responses. To address this problem, luminescent metal-organic frameworks (LMOFs) were introduced. The selected LMOFs respond to analytes two dimensionally (2D): both the emission peak wavelength (x) and the peak intensity (y) change due to analyte-LMOF interaction. Utilizing this strategy, each analyte can be pinpointed on a 2D map, leading to improved selectivity and sensitivity. The response mechanism was studied both experimentally (IR) and theoretically (DFT).