

NIST Spectroscopy Beamline Suite: Soft and Tender X-ray Spectroscopy and Microscopy (100 eV to 7.5 keV canted sources) Three-Letter Acronym (SST-Spectroscopy Soft and Tender)	
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**NIST NSLS-II Spectroscopy Beamline Suite:
Materials Measurement to
Promote Innovation and Industrial Competiveness**

Executive Summary: The National Institute of Standards and Technology (NIST) and the Department of Energy (DOE) have a 30 year ongoing partnership at the National Synchrotron Light Source (building to NSLS-II) developing advanced synchrotron measurement methods and delivering excellence in material science impacting important societal challenges in energy, health, environment, and national security improving our quality of life. This partnership promotes innovation and enhances US industrial competitiveness for inorganic and organic semiconductors, photovoltaics, SAMs, biological and environmental materials, batteries, catalysts, fuel cells, polymers, superconductors, ferroelectrics, and ferromagnets. Located at the NSLS, the NIST Synchrotron Methods Group of nine operates a suite of three state-of-the-art spectroscopy beamlines (U7A, X24A, and X23A2) that span the entire absorption-edge energy range of the periodic table to establish structure function relationships in advanced materials. More than 200 industry and academic researchers each year use the NIST Beamline Suite to accelerate the development of new materials into devices and systems with advanced functionality for a broad spectrum of industries. Building upon this success, NIST proposes to establish an NSLS-II spectroscopy suite of three state-of-the-art high throughput beamlines (with X-ray Diffraction capability) described in two beamline development proposals; *Soft and Tender X-ray Spectroscopy and Microscopy (100 eV to 7.5 keV canted sources)* and *Hard X-ray Absorption Spectroscopy and Diffraction (4.5 keV to 40 keV three-pole wiggler source)*. Taken together, the NIST NSLS-II Spectroscopy Beamline Suite will be capable of measuring the electronic, chemical, and structural properties of almost any material, often at the nanoscale. NIST is committed to fully funding the construction of its proposed Spectroscopy Beamline Suite and to continuous world leading improvements in synchrotron measurement science and technology. Furthermore, NIST will build upon its NSLS based Synchrotron Methods Group to fully staff its stakeholder relationship in NSLS-II.

A. Science Case: Soft and Tender X-ray Spectroscopy and Microscopy (100 eV to 7.5 keV)

Synchrotron based X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy are complementary techniques, probing occupied and unoccupied density of states respectively. The ability to perform both measurements on the same sample achieves a complete, non-destructive, depth selective measurement of electronic structure, chemistry, and bond orientation. *NIST proposes to build a pair of spectroscopy beamlines based on two canted undulator sources, one for soft x-rays (100 eV to 2.2 keV) and one for tender x-rays (1 keV to 7.5 keV).* The beamlines will have a total of 6 unique world class NEXAFS/XPS experimental stations (2 full field microscopes, 2 automated high-throughput, and 2 insitu high pressure); three will be served by the soft x-ray undulator and three by the tender x-ray undulator, thus a variety of soft and tender spectroscopy experiments can be accomplished simultaneously in this beamline complex. Two of the experimental stations (high-throughput XPS/NEXAFS and the XPS microscope) can utilize the soft and tender X-ray undulators (sequentially or even simultaneously) enabling a continuous selection of X-rays from 100 eV to 7.5 keV (at a common focal point) in a single experiment (unique capability, enhancing depth selectivity in XPS; i.e. in Hard X-ray Photoelectron Spectroscopy - HAXPES).

Enabled by the world class brightness of the proposed NIST NSLS-II canted undulator beamline pair, NIST is pioneering (at NSLS) two new and unique (large depth of field for practical materials) magnetic projection microscopes pushing the state-of-the-art in synchrotron XPS and NEXAFS spectroscopy full field imaging measurement science (details in appendix, page 13). (1) XPS microscope; combines nanometer scale spatial resolution with chemical and electronic state specificity and full three-dimensional mapping of the structure of nanomaterials and nanodevices at all points within their volume. (2) Large Area Imaging NEXAFS Microscope for high efficiency, highly parallel spectroscopic chemical and orientation maps of gradient samples, combinatorial arrays (e.g. 1000s of compositional samples at a time), and device arrays up to 4 cm² with simultaneous micron scale resolution.

The proposed *Soft and Tender X-ray Spectroscopy and Microscopy* beamline pair coupled with NIST's continuous development of automated high-throughput spectroscopy methods, world class high efficiency detectors, and unique NEXAFS and XPS microscopes will have a *large scale impact on the materials science of important societal challenges in energy, health, environment, and national security.* Some strategic science case examples follow. They illustrate how this proposed beamline pair will establish structure function relationships in advanced materials, often at the nanoscale, to accelerate the development of new materials into devices and systems with advanced functionality for promoting innovation and enhancing US industrial competitiveness.

- 1) Accelerating Organic Photovoltaics with Soft and Tender Spectroscopy and Microscopy
Dean M. DeLongchamp, NIST
- 2) Nanoscale Spectroscopy for Next Generation Semiconductor Microelectronics: CMOS and Beyond
Pat Lysaght, SEMATECH

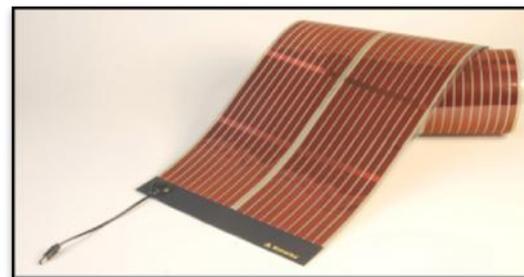
Additional Science Case Examples (3-13) appear in the appendix page 13:

- 3) Designing Biomaterials with High Through-Put Screening: Using the NIST NEXAFS Microscope
David Castner (U. of Washington, Seattle)
- 4) Synchrotron Spectroscopy an Enabling Capability for the Defense and National Security Community
Joseph Lenhart (WMRD, US Army Research Laboratory)
- 5) Nano to Microscale Spectroscopy for Environmentally Friendly Marine Anti-Fouling Coatings
Edward Kramer (UCSB)
- 6) Spectroscopy and Microscopy for Advanced Hard and Soft Materials: Energy and Microelectronics
Gary Mitchell (Dow)
- 7) Advanced Spectroscopy Promoting Breakthrough Catalysts for Energy Applications
Simon Bare (UOP)

Accelerating Organic Photovoltaics with Soft and Tender Spectroscopy and Microscopy

Dean M. DeLongchamp (NIST)

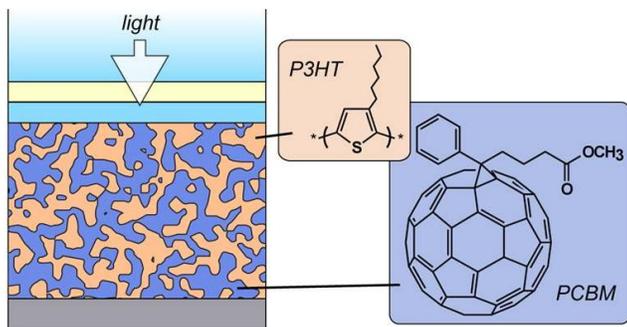
Affordable, renewable power generation, a critical component of U.S. energy independence, has remained for many years perpetually on the threshold of technical and economic viability. The largest solar power development efforts have focused on incremental improvements of older technologies, and even with these efforts, photovoltaics still produce less than 0.05 % of our national electrical energy needs.¹ New solar energy technologies, such as organic photovoltaics (OPV), promise to break this paradigm by greatly reducing both the manufacturing costs and the capital required to increase production.² The active layers of an OPV module are formulated as liquid inks that can be applied to flexible surfaces using simple graphics arts printing techniques such as inkjet, spray, and screen printing, to create solar cell modules that can be spread over large areas as easily as unrolling a carpet. The commercialization of OPV technology has been slowed by two key technical challenges: enhancing the power conversion efficiency, and preventing aging-related performance loss. To address these challenges requires precise measurements of materials composition and molecular orientation with sub-100 nm spatial resolution.³ These needs will be met by *NIST's new soft and tender X-ray microscopes and beamlines* described in this NSLS-II proposal, which promises to greatly accelerate the development of high-efficiency, long-lasting solar modules with the potential to build a new domestic solar cell manufacturing industry in the U.S. and transform our energy production landscape in the coming decades.



Konarka's Power Plastic[®] organic photovoltaics module. NIST has an active CRADA with Konarka (Lowell, MA).

The power conversion efficiency of bulk heterojunction (BHJ) OPV devices critically depends on the distribution of the polymer absorber and the fullerene electron acceptor (e.g., the blend morphology).⁴ Synchrotron-based tools provide a critical means to probe the structure of the BHJ layer. For example, NIST recently applied Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy to reveal that the vertical distribution of BHJ components follows segregation behavior similar to that of miscible polymer blends. The top (air) interface becomes rich in the polymer absorber, whereas the bottom interface depends on the substrate.⁵ This effect greatly impacts charge carrier mobility measurement; transistors fabricated from BHJs can exhibit ambipolar or hole-only transport depending on the dielectric. These results were extended to

practical photovoltaic devices by comparing BHJs cast upon hole transport layers that have similar work functions but different surface energies.⁶ The molecular orientation of the absorber revealed by NEXAFS contributed to the development of accurate optical models for the practical devices. This work illustrates the importance of non-destructive interface measurements via *high-throughput, automated NEXAFS* to the acceleration of OPV technology development. High-throughput, automated NEXAFS acquisition on 100's of PV samples is required to rapidly build structure function relationships for intelligent PV materials design and processing.



The BHJ active-layer morphology is critical to its power conversion efficiency.

¹ U.S. Energy Information Administration, Electric Power Monthly, May 2010.

² "Organic and Dye-Sensitized Cell Photovoltaics: Materials, Applications, and Opportunities," *NanoMarkets*, 2010.

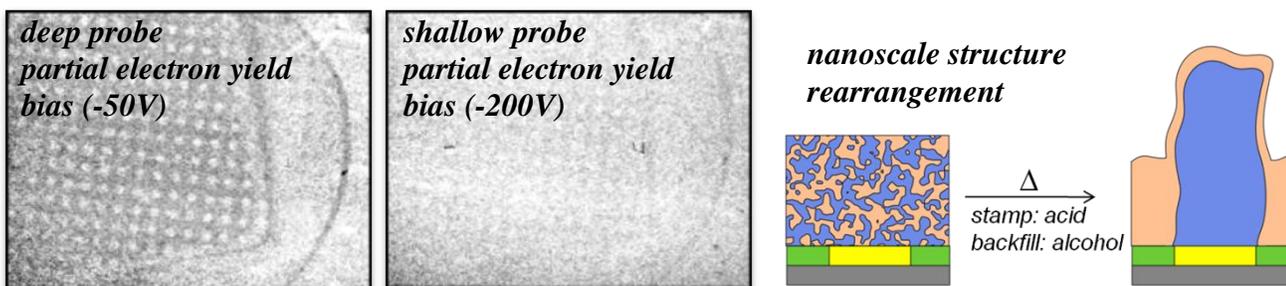
³ NIST Grand Challenges for Advanced Photovoltaic Technologies and Measurements Workshop, Denver, CO, 2010.

⁴ DOE SETP, National Solar Technology Roadmap Organic PV, 2007.

⁵ DS Germack et al., *Applied Physics Letters*, 2009, 94, 233303.

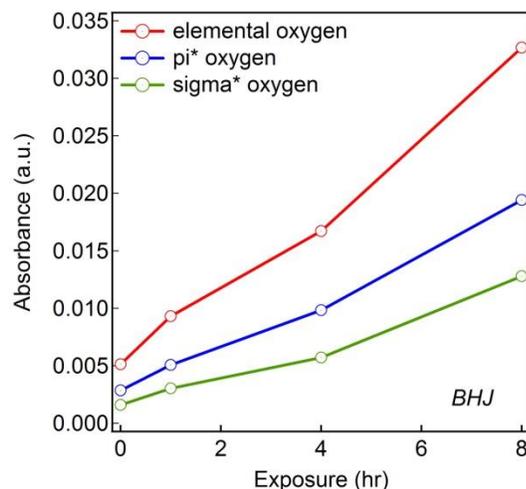
⁶ DS Germack et al., *Macromolecules*, 2010, 43, (8), 3828-3836.

The ideal OPV system has a three-dimensional domain network structure with dimensions less than 100 nm. Small changes to the distributions of domain size and shape strongly impact OPV performance. Composition-sensitive microscopy methods with high spatial resolution are thus critical to the measurement and rapid optimization of OPV active layer structure. To this end, NIST recently demonstrated a new, full-field NEXAFS microscope (at NIST's U7A beamline) that is capable of measuring the three-dimensional compositional structure of OPV films. The images below show a BHJ film "by design" that has been purposefully structured by thermal annealing atop a chemically patterned template. The fullerene component is attracted to the high energy acid surface (yellow), whereas the polymer absorber is attracted to the lower energy alcohol surface (green). The powerful depth resolution of NEXAFS microscopy is revealed by comparing images collected at shallow and deep bias conditions. The loss of contrast at the shallow condition reveals that the surface is covered with a ~ 2 nm thick "skin" of the polymer. This information is required to understand and eventually control the three-dimensional domain structure of OPV active layers. Although compelling, the images shown below are proofs-of-concept with a $\approx 300 \mu\text{m}$ diameter stamp; the sub-micron resolutions of the proposed **Larger Area Imaging NEXAFS Microscope** and **XPS (3D-Chemical) Microscope** are required to approach lateral resolutions that are relevant to the frontiers of OPV technology. Whereas the XPS microscope will provide the most powerful measurement of domain structure, the NEXAFS microscope will be required to determine how variations in composition are correlated to variations in local orientation, which is critical to local photon absorption and nanoscale exciton / charge carrier transport processes.



NIST's NEXAFS microscope (NSLS U7A) reveals the structure of an OPV film structured "by design" in collaboration with University of Washington (Ginger). Lighter areas are fullerene-rich; contrast is generated by split π^* resonance of fullerene.

NEXAFS and XPS microscopy will also impact OPV technology development in the measurement of aging-related performance loss. High vertical and lateral resolutions are required to determine the precise locations of chemical degradation products. **The unique 100 eV to 7.5 keV energy range of the NIST NSLS-II Spectroscopy Beamline Suite** will provide unprecedented depth selectivity to measure the vertical distribution of degradation products near interfaces. Recent NEXAFS measurements (at NIST's U7A beamline) have shown the technique to be quite sensitive to oxygen incorporation in OPV materials. The polymer absorber is found to be chemically vulnerable at the point where a side chain is added to enhance solubility and aid processing. Oxygen π^* and σ^* resonance intensities increase commensurately, indicating a carboxyl-containing oxidation product. By nondestructively identifying the mechanisms of degradation, and their location within devices, these tools will greatly accelerate the development and deployment of robust, high-efficiency plastic solar cells.



NEXAFS measurement of oxygen incorporation into an OPV active layer.

Nanoscale Spectroscopy for Next Generation Semiconductor Microelectronics: CMOS and Beyond
 Pat Lysaght (SEMATECH)

SEMATECH is a non-profit consortium established more than 20 years ago to perform basic research in semiconductor manufacturing. In recent years, the consortium of leading semiconductor manufacturers has set global direction and bridged strategic R&D to manufacturing with a business model based on highly flexible collaboration and demonstrated internal information control. Today, SEMATECH continues accelerating the next technology revolution with nanoelectronics and emerging technology partners including federally funded research initiatives that directly enhance applications in information technology, communications, medicine, energy, and national security. To this end, SEMATECH has engaged in collaboration with the NIST Synchrotron Methods Group stationed at the NSLS and during the past 6 years has conducted state of the art research at each of NIST's three NSLS spectroscopy beamlines for materials screening and optimization research: X23A2, X24A, and U7A for EXAFS, high-energy XPS, and NEXAFS. Two current examples of DARPA funded SEMATECH programs include: i) Sub-threshold-slope Transistors for Electronics with Extremely-low Power (STEEP) and ii) Carbon Electronics for RF Applications (CERA).

The STEEP program goal is to develop a revolutionary transistor technology for logic circuits with extremely low power consumption while maintaining high performance for logic applications in areas such as unattended sensors with unlimited lifetimes or autonomous unmanned air vehicles navigated by vision systems. The key technical challenges of achieving steep-sub threshold-slopes over many decades of current; developing novel circuit designs accommodating asymmetric source-drain regions; demonstrating abrupt doping profiles at tunneling junctions; and integrating SiGe, Ge, or III-V compound semiconductors in transistor structures to facilitate the required tunneling currents – all require the most advanced analytical tools equipped with the highest spatial resolution available to assure success. **SEMATECH is extremely excited anticipating process optimization results from samples studied via the new NIST NSLS-II soft and tender beamline pair for NEXAFS, high energy XPS, and chemical imaging.** These new capabilities will uniquely impact the STEEP and other SEMATECH programs by enabling simultaneous nanoscale spatial resolution and depth selectivity (via variable kinetic energy high-energy XPS in the range of 100 eV to 7.5 keV) essentially operating as a rapid, **non destructive 3D XPS microscope at the nanoscale.**

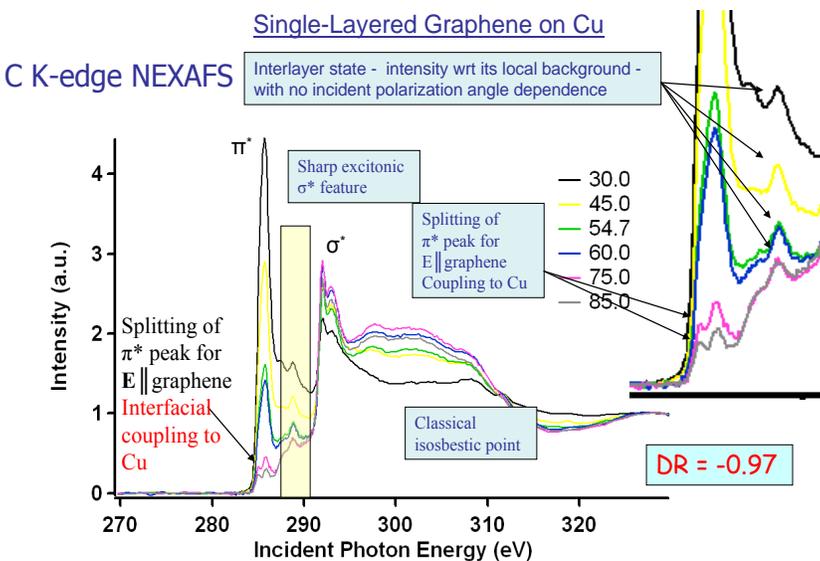


Figure 1. Polarization dependent NEXAFS spectra of single layer graphene on Cu foil which illustrates evidence of π^* splitting (at high polarization angles) and the interlayer state (inset).

The CERA program targets development of wafer-scale graphene synthesis focused on enabling ultra-high-speed, low-power graphene-channel field-effect transistors through innovative approaches that enable revolutionary advances in materials science, epitaxial growth, transistor development, and RF circuit design. The research needed to achieve the goals of the CERA program is another area where NIST's proposed advanced synchrotron spectroscopy imaging techniques and advanced measurement instruments are pivotal to success. An example of the **critical need for high-throughput low energy polarized NEXAFS** as a probe for characterizing the electronic structure of graphene has recently been demonstrated in University of Buffalo-SEMATECH-NIST collaboration on NIST beamline U7A at the NSLS, which resulted in a publication on Cu/graphene substrate

hybridization [1]. Figure 1 illustrates the best resolved splitting (reported in the literature) of the π^* absorption feature and indisputable evidence for the existence of an interlayer state that has been the subject of sharp debate for more than 20 years. These exciting results have stimulated the collaborative interest of theorists and modeling and simulation of the NEXAFS spectra is in progress.

In addition to the STEEP and CERA programs, all of the planar and non-planar CMOS logic and non-volatile memory device programs at SEMATECH are materials limited and critical challenges associated with continued scaling have *demonstrated a clear and urgent need for both of NIST's proposed microscopes (nano and micro scales)*.

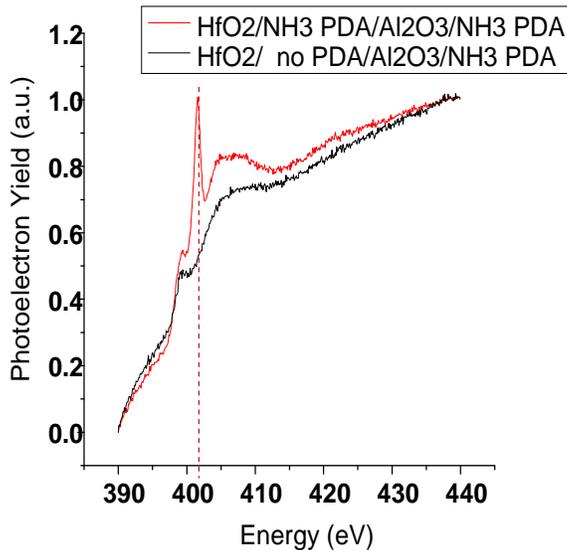


Figure 2. Surface sensitive N K edge absorption spectra shows that Al in-diffusion into HfO₂ (black curve) is limited when HfO₂ is preannealed in NH₃ ambient, evident by surface Al-N peak (red) [2].

For example, there is a universal need to identify surface chemical states as a function of processing as achieved recent *NEXAFS results from NIST beamline U7A* (HfO₂/Al₂O₃, probing the outermost 1 nm of material as shown in fig. 2).

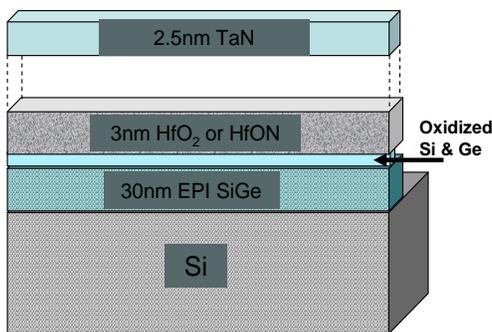


Figure 4. Material stack measured by high-energy XPS (a-d) on NIST beamline X24A at the NSLS. Acquisition of bulk sensitive (Si 2p, Ge 3d) and surface sensitive (Si 1s, Ge 2p) core lines allows the oxidation kinetics as a function of processing to be determined.

Also to determine the corresponding changes in binding energies of chemical constituents

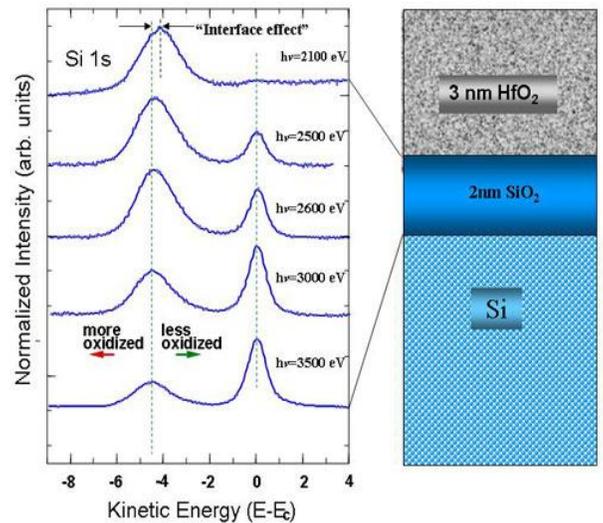
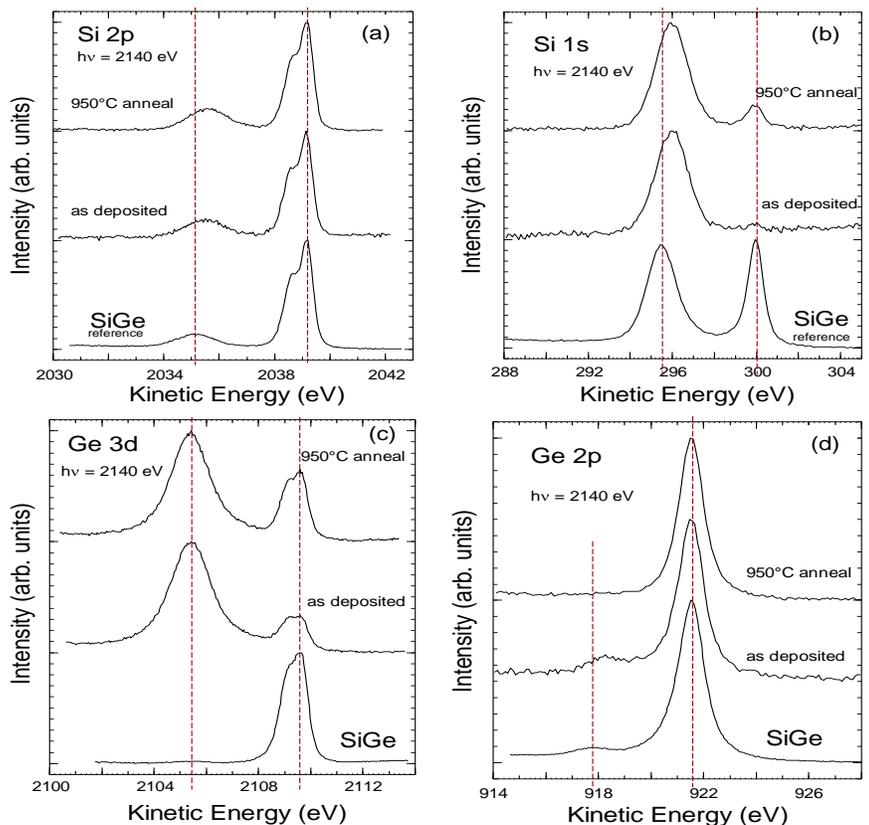
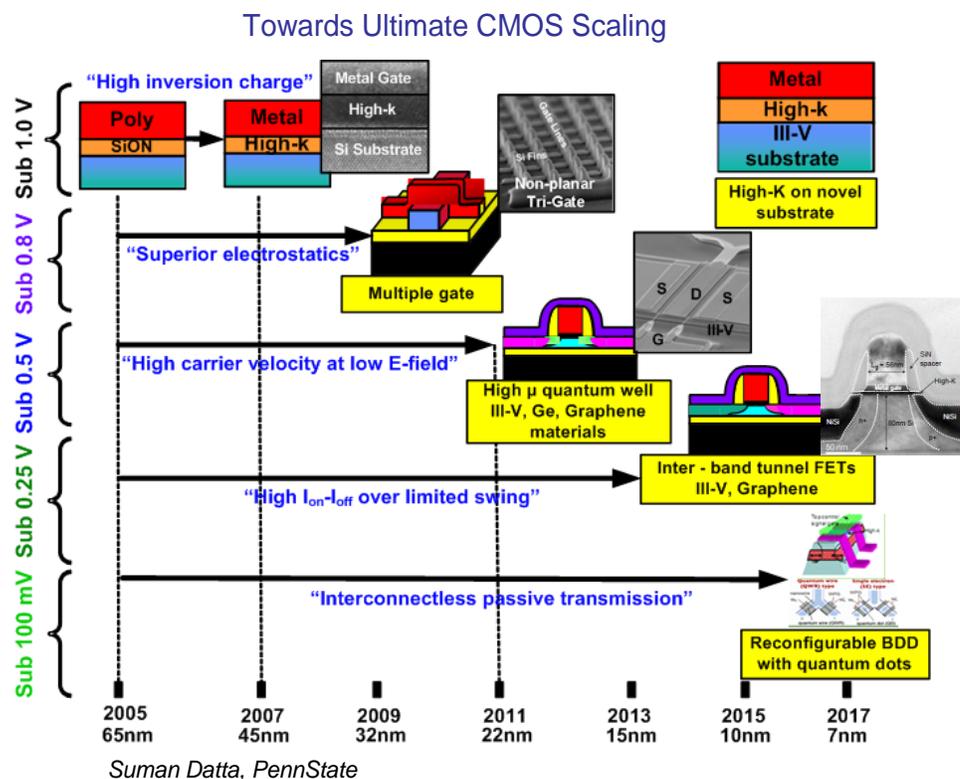


Figure 3. Si 1s spectra from 3nm HfO₂/2nm SiO₂ sample recorded with variable kinetic energy high-energy XPS (VKE-XPS) illustrates depth profiling and an interface effect near HfO₂/SiO₂ interface [3].



of buried layers and interfaces as measured with *tender XPS on NIST beamline X24A* ($\text{HfO}_2/\text{SiO}_2$, shown in fig. 3) and detecting variations in oxidation state of underlying engineered substrate elements (SiGe, shown in fig. 4), in order to ultimately explain the mechanisms that give rise to the limits of electrical performance. All these examples have a common need for spectroscopy of large numbers of samples generated by numerous materials and processing parameters, *NIST's proposed NSLS-II soft and tender beamline pair and high-throughput NEXAFS/XPS stations answer this challenge.*

An example of the diverse and challenging device architectures and novel film systems verses power that are slated for manufacturing on a timeline according to *The International Technology Roadmap for Semiconductors 2009 edition* are given below.



These architectures are currently being researched (many with no known solution). *The proposed NIST XPS microscope with nano-scale spatial resolution is ideally suited to the timeline* construction and materials (65 nm down to 7 nm resolution).

Continued collaborative access with NIST is critical to the success of SEMATECH as a pioneer of new technologies.

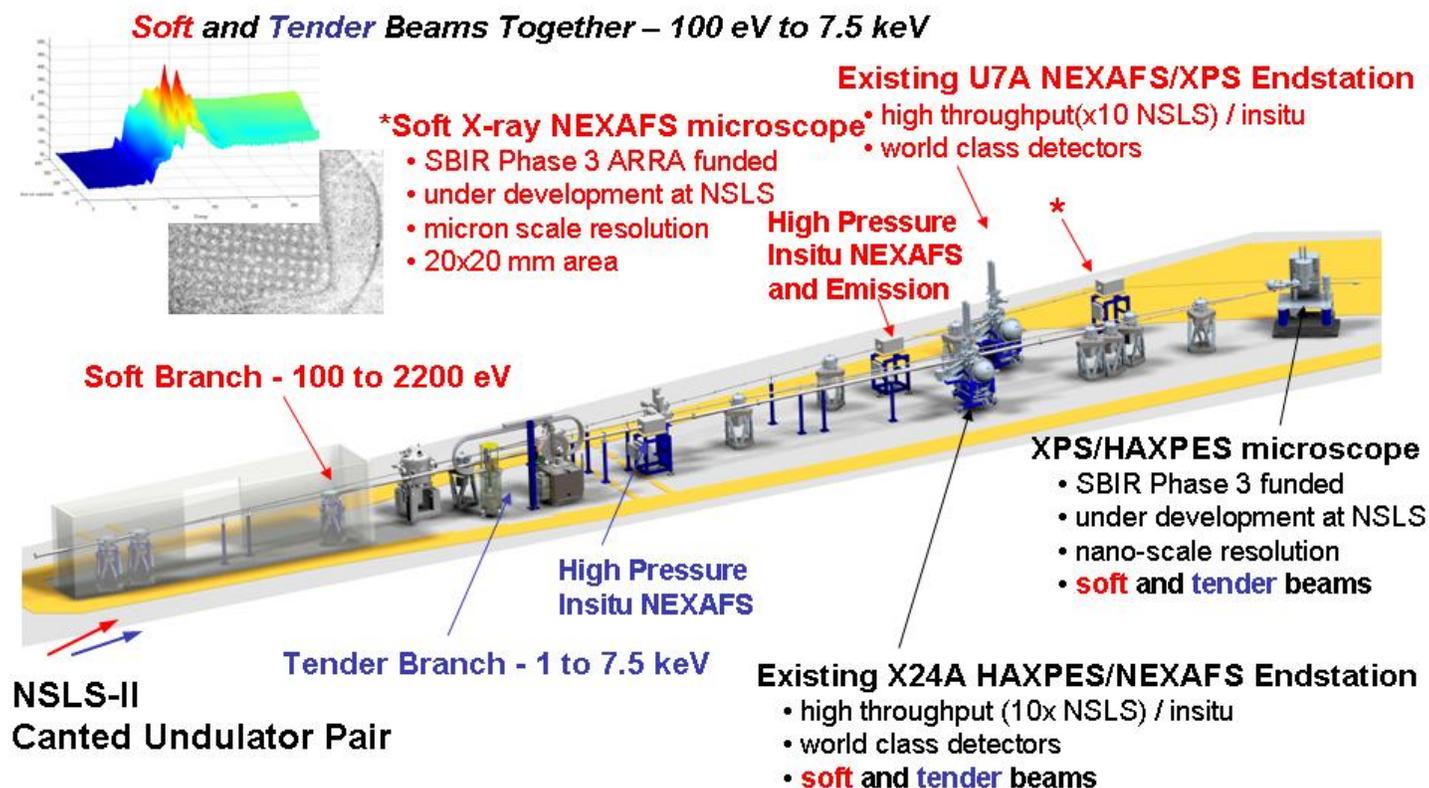
1. S. Banerjee, et al. *J. Phys. Chem. Lett.* 1, 1247–1253, (2010).
2. P. Lysaght, et al. *International Journal of Materials Research (IJMR)* June, (2009).
3. P. Lysaght, et al. *J. Appl. Phys.* 101, 024105 (2007).

B. Beamline Concept & Feasibility

NIST proposes to build a pair of spectroscopy beamlines served by two insertion devices canted at an angle of 2 mrad: a 2.5 m long APPLE II device for 100–2200 eV (soft x-rays) and a 1.5 m in-vacuum undulator covering the range 1.5–7.5 keV (tender x-rays). The newly developed full field XPS microscope requires a spot size of 10 microns over the full energy range of both beamlines and mandates to locate the insertion devices at a low beta straight section of NSLS-II. The undulator sources are imperative to deliver adequate brightness and flux for the microscopes, high resolution XPS, soft x-ray fluorescence yield NEXAFS and emission spectroscopy, and high-throughput (>10 times NSLS) electron yield NEXAFS.

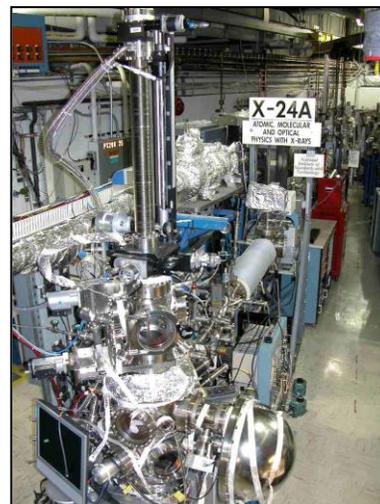
The soft x-ray beamline is based on a variable line spacing plane grating monochromator (VLSPGM) capable of delivering a resolving power higher than 2×10^4 over its full energy range (FMB Oxford, NIST contact awarded FY08). The tender x-ray beamline is based on an extended range (theta -3° to 85°) double crystal monochromator (LN_2 cooled DCM) equipped with YB66, Si(111) and (220) crystals to achieve medium and high resolution 333 reflection near normal (FMB Berlin, NIST contact awarded FY09). The expected flux in all experimental stations of the beamline pair will be in the range 10^{12} – 10^{13} photons/s with resolving powers between a few thousands and 10^4 . A complete optical design including ray tracings, spot sizes and expected fluxes at each of the experimental stations will be available upon request.

The beamline pair will have 6 unique world class NEXAFS/XPS experimental stations as shown schematically below; red and blue denote which stations will receive soft and/or tender x-rays, respectively. The automated high-throughput HAXPES/XPS/NEXAFS station and XPS/HAXPES microscope utilize both monochromatic soft and tender beams enabling a continuous selection of X-rays from 100 eV to 7.5 keV at a common focal point in a single experiment (unique capability, enhancing depth selectivity in XPS or HAXPES). Computer controlled mirrors and pass-through beams are used to rapidly switch soft and tender x-rays between the 6 stations to fully utilize and optimize all the available beamtime (an extension of NIST's NSLS U7A beamline operation among 4 endstations). The high energy limit (7.5 keV) was chosen so that the two beamlines could operate hutch-less (see CAD model below)



XPS Microscope Station (pictured at left, details in appendix, page 13) - This new XPS microscope is under development at NSLS (U4A). It is an SBIR Phase-III collaboration between NIST and *R. Browning Consultants*. To date, 4 Patents have been granted for this new microscope technology. At NSLS-II it will receive soft and/or tender beams via two KB mirror pairs that have a common focal spot of 13 μm . The new XPS microscope can be thought of as a super conducting magnetic projection lens x-ray photoemission electron microscope (XPEEM). The full field magnetic projection lens enables large depth of field nanoscale spatial and spectral XPS imaging over the full range of kinetic energy (100 eV to 7.5 keV) tuning the sensitivity from surface to bulk length scales ideally suited for photovoltaics and microelectronics. There are no high voltages; samples can be rough or insulating. Thus the XPS microscope, combines nanometer scale spatial resolution and depth selectivity with XPS chemical and electronic state specificity to enable full three-dimensional (3D) chemical mapping of the structure of nanomaterials and nanodevices at all points within their volume.

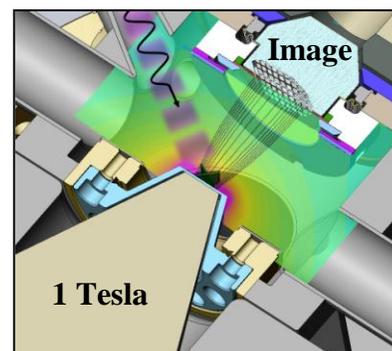
Existing X24 HAXPES/ NEXAFS Station (pictured at right) is the only hard x-ray photoelectron spectroscopy (HAXPES) facility in the United States and is in high demand for microelectronics interfacial characterization (e.g., SEMATECH). This automated high-throughput station has a load lock system capable of holding up to 100 samples at a time and a High Energy Scientia 4000 electron analyzer. Additionally, for NEXAFS it has large solid angle electron yield detector and a 7-element Ge ultra high resolution x-ray detector for soft and tender x-ray fluorescence yield. This HAXPES/XPS/NEXAFS station will be transferred to NSLS-II where it will receive soft and tender x-rays (100 eV to 7.5 keV) at a common focal point of less than 100 μm with intensity to enable at least a 10x gain in sample throughput over operation at NSLS X24A and improved X-ray energy resolution using near normal incidence Si(333) crystals.



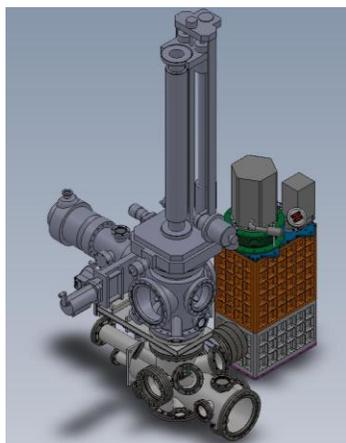
Existing U7A NEXAFS/XPS Station (pictured at left) is under 24/7 use for OPVs, nanomaterials, biomaterials, batteries, polymers and polymer interfaces (see science case examples). This automated high-throughput station has a load lock system capable of holding up to 100 samples at a time and a Scientia Wide Angle 4000 electron analyzer. For Electron Yield (EY) NEXAFS it has a large solid angle EY detector and a novel 36 channel detector array for measuring EY at all takeoff angles and at all angles of x-ray incidence simultaneously for high-throughput NEXAFS depth profiling of surface treatments in advanced materials. For Fluorescence Yield NEXAFS it has a 14-element ultra high resolution Si(Li) x-ray detector and a unique focusing graded multilayer mirror and proportional counter for ultra low background FY NEXAFS; e.g., reaction intermediates in catalysts. This NEXAFS/XPS station will be transferred to

NSLS-II where it will receive soft x-rays (100-2200 eV) at a focal point of less than 100 μm with intensity to enable at least a 10x gain in sample throughput over operation at NSLS U7A. A dithering system will allow mm spot sizes when performing NEXAFS on radiation sensitive samples.

Large Area Imaging NEXAFS Microscope Station (pictured schematically at right, with details in appendix page 13) is a working prototype station at NIST's U7A beamline. It is a highly efficient 1 Tesla magnetic projection partial electron yield full field microscope imaging 13x18 mm at 50 μm spatial resolution with a large depth of field (rotatable sample see figure a right). The microscope has been used to image combinatorial arrays of SAMs, batteries, OPV and various designer surfaces (see science case examples). This automated high-throughput prototype NEXAFS imaging station has a load lock system capable of holding up to 10 samples at a time. An ARRA funded (FY09 NIST SBIR Phase III with *Synchrotron Research, Inc.*) superconducting magnet (8T) NEXAFS microscope for NSLS-II is under development, to be commissioned at NSLS U8B beamline.



The new superconducting microscope will produce highly efficient, highly parallel spectroscopic chemical and orientation maps of gradient samples, combinatorial arrays (e.g. 1000s of compositional samples at a time), and device arrays up to 4 cm^2 with simultaneous micron scale resolution. This microscope end station will be transferred to NSLS-II and will receive soft x-rays (100-2200 eV) from a pair of dithered mirrors providing 4x4 cm high flux sample illumination.



Existing U7A High Pressure Insitu Soft X-ray NEXAFS and Emission Station (pictured schematically at left) is a prototype station at NIST's U7A beamline. NIST is pioneering a 10 mm² area, 256 element, micro-calorimeter soft x-ray detector that will be capable of better the 1 eV resolution at 25 kHz count rate (details in appendix, page 13) for low background FY NEXAFS and soft x-ray energy dispersive emission spectroscopy. This automated high-throughput station has a load lock system capable of holding up to 100 samples at a time. High pressure capability will be achieved with windows and cells that are in routine use in soft x-ray microscopy. This station will be transferred to NSLS-II where it will receive unfocused soft x-rays (100-2200 eV) with spot size of 1 mm².

High Pressure Insitu Tender X-ray NEXAFS/XAS Station to be developed. The station will have FY and EY detectors, high pressure and insitu operation to be achieved with standard windows and cells. Insitu catalytic studies of sulfide and chloride reaction intermediates will be routine in this station. At NSLS-II this end station will be located just down stream of the tender monochromator where it will receive unfocused tender x-rays (1-7.5 keV) with a spot size of 1 mm².

C. Required Technical Advances (if any)

No beamline technical advances are required to achieve the level of performance in this proposal. The soft and tender beamline optical design is complete, including the common focal point at two experimental stations for continuous 100 eV to 7.5 keV operations. The two new NIST full field microscopes (NEXAFS and XPS) are fully funded, developing quickly and will be ready for the start of NSLS-II.

D. User Community and Demands

XPS and NEXAFS spectroscopies have a large and growing user base as evidenced by the development of state of the art spectroscopy (and microscopy) insertion device beamlines at 3rd generation synchrotrons throughout the world. In particular, here at NSLS (building to NSLS-II) NIST's existing spectroscopy beamlines (soft U7A, tender X24A, and hard X23A2) have oversubscribed general user programs. All the NIST *Participating Research Team* (PRT) beamtime is fully utilized for NIST scientific collaborations (fundamental and applied materials science) and advanced measurement method development (detectors, high-throughput automation, and microscopy). ***The breadth, diversity, and demands of NIST's user community that consists of 25 Industrial, 25 Academic, and 14 National Laboratory Scientific Groups (complete list in appendix page 13) are highlighted in the proposal selected Science Case examples.***

The anticipated strong user demand for NIST's proposed *Soft and Tender X-ray Spectroscopy and Microscopy (100 eV to 7.5 keV) canted undulator beamline pair* is based in part on the existing NSLS user base established at U7A (16 years) and X24A (6 years) for NEXAFS and XPS/HAXPES respectively and documented user needs from various recent workshops. NSLS and NSLS-II conducted a series of workshops in early 2008 as part of the process of gathering community input to form the strategic scientific plans for beamline development at the two facilities. NIST's NSLS-II beamline plans for spectroscopy and microscopy were endorsed and promoted in three of the resulting white papers (representing about 150 scientists) ; *Chemical and Energy Sciences, Soft and Biomolecular Materials, and Hard Condensed Matter and Materials Physics*. NIST chaired an *International Workshop for New Opportunities in Hard X-ray Photoelectron Spectroscopy: HAXPES 2009* (sponsored by NIST, NSLS, NSLS-II, and BNL Condensed Matter Physics). This three-day workshop brought

together approximately 100 scientists from 14 countries to discuss progress and future prospects for this rapidly developing field of research and included sessions devoted to industrial use of HAXPES. Currently, NIST's NSLS X24A beamline is the only United States HAXPES facility; the workshop made a compelling strategic case for NIST's investment in a state of the art undulator NSLS-II beamline for HAXPES and microscopy. In particular, for industrial applications (*real samples from the real world*) such as layered structures this is exemplified in the SEMATECH Science Case (page 5) by Pat Lysaght *Nanoscale Spectroscopy for Next Generation Semiconductor Microelectronics: CMOS and Beyond* (tuning the length scale of XPS).

Brookhaven National Laboratory hosts the Joint Photon Science Institute (JPSI), which brings together Industry, National Laboratories, and Universities to catalyze innovation using synchrotron radiation at NSLS-II. NIST is a founding member of JPSI and Dr. Chi-Chang Kao is the Director (and a member of this proposal's Science and Technology Advisory Panel). Over the past year, JPSI has held *NSLS/NSLS-II New Opportunity Workshops in Microelectronics, Batteries, and Photovoltaics*. Each of these workshops has brought together technology and academic leaders (total of 150) who see NIST's proposed NSLS-II spectroscopy beamlines as an important key to solving some of the Nation's most challenging problems (see attached JPSI letter of endorsement from Dr. Chi-Chang Kao in the appendix, page 13).

XPS (or ESCA) is a fully established and widely used surface chemical analytical technique with in house XPS laboratory instruments at most major university, national, and industrial laboratories. Commercial XPS microscopes (5 micron resolution) are also often included; e.g. NIST Gaithersburg has two. These laboratories represent substantial capital and staff investment, speaking strongly to the importance and impact of XPS in the general scientific material science community. This large and well-developed laboratory based XPS user group is a nearly untapped community that will be brought to NSLS-II (although NIST has made a good start e.g. SEMATECH, Dow, GE, UOP, Sandia and BNL). In this beamline proposal, NIST's synchrotron based XPS offers the existing lab based community unique depth selectivity (continuous selection of X-rays from 100 eV to 7.5 keV in a single experiment), automated high-throughput sample handling, and nanoscale XPS microscopy. Our XPS user base has enthusiastically endorsed NIST's NSLS-II XPS plans embodied in this proposal (see the individual Science Case examples).

E. Proposal Team Expertise and Experience (*not included in page count*)

The Proposal Principal Team Daniel Fischer (project director), Joseph Woicik, and Bruce Ravel are members of NIST's Synchrotron Methods Group of 9 staff (all located at the NSLS fulltime, Fischer is the group leader) that currently run 3 NIST PRT Spectroscopy Beamlines (U7A, X24A, X23A2) and 2 NIST *Measurement and Instrument Development Team* (MIDT) Beamlines for each of the NIST' NSLS-II microscope development projects. These NIST staff members represent a permanent and growing investment by NIST in developing and operating beamlines at NSLS-II (Type-II beamline development). Fischer, Woicik, and Ravel are senior members of the technical staff and are all highly regarded scientists within the NIST institution. The Proposal Principal Team has significant and highly successful direct beamline experience building, developing, maintaining, and managing spectroscopy user facilities, continuously improving measurement capabilities, and producing excellent science spanning nearly three decades. They are all highly respected members of the synchrotron community and are valued NIST ambassadors to the DOE at the NSLS (and NSLS-II). The team often represents the user community on the NSLS User Executive Committee and numerous NSLS and DOE advisory teams and review panels. *A one page brief bio of each Principal Proposal Team member appears in the appendix (see page 13).*

F. Suggestions for BAT Membership (*not included in page count*)

Science and Technology Advisory Panel: all listed on page 1 (*not included in page count*) have agreed to serve

G. Funding and Management *(not included in page count)*

NIST NSLS-II Soft and Tender Beamline Total Capital Investment to Date: \$10 million
(Details outlined below)

Existing U7A fully automated world-class soft x-ray spectroscopy station	\$2,000K
Existing X24A fully automated world-class tender x-ray spectroscopy station	\$1,500K
Large Area Imaging NEXAFS Microscope station (ARRA FY09 funding, NIST SBIR Phase III)	\$2,500K
XPS Microscope station (SBIR Phase III ongoing funding)	\$1,500K
Existing U7A High Pressure In situ Soft X-ray NEXAFS and Emission Station (NIST developed 256-element transition edge detector)	\$1,500K
Varied Lined Spacing Plane Grating Monochromator (FMB Oxford contact awarded FY08)	\$500K
Tender Double Crystal Monochromator, LN ₂ cooled ((FMB Berlin contact awarded FY09)	\$500K

NIST NSLS and NSLS-II Funding and Staffing Overview: NIST is committed to fully funding the construction of its proposed Spectroscopy Beamline Suite and to continuous world leading improvements in synchrotron measurement science and technology. NIST will build upon its NSLS based Synchrotron Methods Group to fully staff our stakeholder relationship in NSLS-II to develop the proposed NSLS-II Spectroscopy Beamline Suite.

NIST NSLS-II Beamline Development Approach Overview: (1) Finish optical design and specification of all mirrors. (2) Develop a detailed beamline conceptual design including cost and schedule. (3) Develop a beamline organizational and management system. (4) Develop a full Beamline Project Execution Plan in coordination with NSLS-II management and staff.

NIST Transition Plan to NSLS-II Overview: (1) Maintain NIST's leading role in synchrotron materials measurement science together with our partners as fully committed long time stakeholders at the NSLS moving to an operational NSLS-II. (2) As soon as possible, begin assembling and commissioning on the floor of NSLS-II a new NIST Spectroscopy Beamline Suite teaming with expert contractors to leverage our NIST group at NSLS. (3) Strategically move NIST's NSLS state-of-the-art endstations to their new NIST NSLS-II beamlines, thereby minimizing down time.

Appendix

Part A Science Case continued: *Science Case examples highlighting materials science in important societal challenges in energy, health, environment, and national security.*

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Designing Biomaterials with High Through-put Screening: Using the NIST NEXAFS Microscope

David Castner (U. of Washington, Seattle)

Interactions between solid surfaces and the biological environment play an important role in many areas of medicine [1]. Examples include biocompatibility of implants, biomolecule separations, bacterial-induced corrosion and biosensors. When biomaterials such as implants are exposed to biological media their surfaces will rapidly be covered by a monolayer of adsorbed proteins [2] followed by attachment of cells (neutrophils, macrophages, etc.). Since the nature of the surface can strongly influence the structure and orientation of the adsorbed protein layer, which in turn can affect the subsequent cellular interactions, understanding the structure of surfaces and the nature of adsorbed protein films are key links in understanding interfacial biology. Similarly, for biosensors, the effectiveness and activity of the sensor depends on the orientation and conformation of the surface bound biomolecule. Specifically, DNA, carbohydrate and protein modified surfaces have all received considerable attention in the fields of bio- and nanotechnology due to their importance in the development of biosensors and biomaterials. The development of surfaces with bound DNA, proteins or carbohydrates of known orientation hold the possibility to improve biosensor microarray development, as well as biomaterials that induce normal healing. Microarrays generally involve large areas of micron size spots (see Figure 1 for schematic of typical microarray spot dimensions.) Until recently it has been difficult to get direct chemical information from the actual micron size spot, and large area modifications and analysis have been used to determine the chemistry. NEXAFS is a key technique to provide information about order and orientation within these modified surfaces. Some recent preliminary studies have used NEXAFS (and the capabilities at NIST's beamline U7A at the NSLS) to directly examine the detailed structure and orientation of surface-bound peptides [3-5] and proteins [5,6]. NEXAFS can be used to study increasingly more complex biomolecules (from short chain amino acids to more complex proteins).

The NIST NEXAFS Microscope allows for unprecedented high throughput screening of samples for biomedical applications. We rapidly evaluated different self-assembled monolayer (SAM) preparation methods by imaging arrays of 45 samples with a surface area of 1 mm^2 each (see Figure 2). The spectral information extracted out of just three image stacks taken within three hours was equivalent to the amount of data typically collected during five days of NEXAFS beam time. ***Using the full $20 \times 20 \text{ mm}$ field of view of the new NIST NEXAFS Microscope makes it possible to simultaneously run up to 400 samples.*** This novel, highly parallel data acquisition approach will benefit biomedical

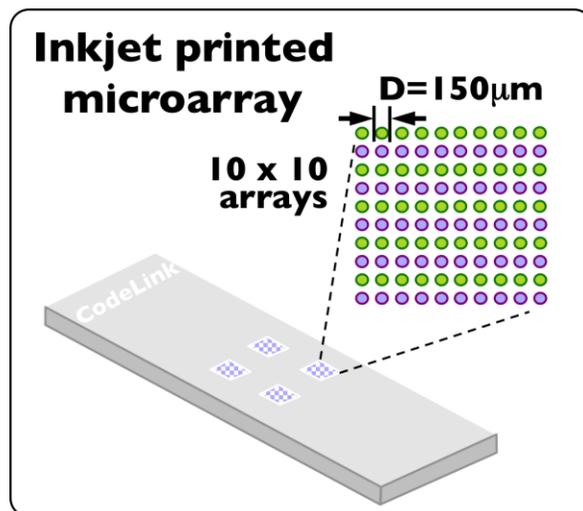


Figure 1: Schematic of DNA micro-array

Bio-combinatorics using NEXAFS

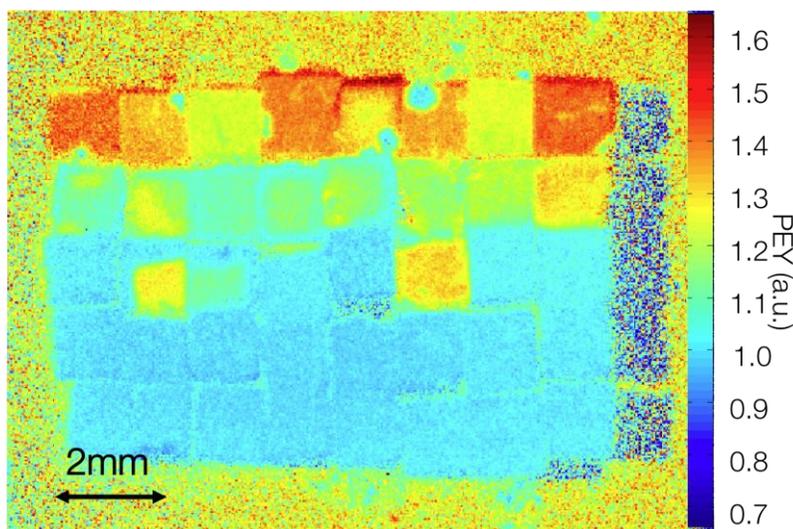


Figure 2: NIST NEXAFS Microscope image of SAM sample array. The contrast is based on signal in the 284.5-285.6 eV X-ray energy band related to aromatic π^* resonances. Azobenzene-terminated self assembled monolayers on gold based on different binding units and backfill strategies were screened for azobenzene surface density.

research tremendously since it allows to test a wide range of preparative conditions and replicates without the need for prohibitively extended beam times. Also, the small scale reduces the amount of biological material needed for sample preparation, a valuable savings for samples where μg quantities of a particular DNA sequence or protein can cost hundreds of dollars.

For nanomedical applications the control of protein orientation is key because the ensemble sizes get extremely small and “every protein counts”. For miniaturization advances to be realized in the nanomedicine field that are comparable to the advances seen in the semiconductor industry, major efforts are needed to optimize protein uniformity within extremely small feature sizes. Techniques such as imaging surface plasmon resonance, IR, Raman and fluorescence microscopy have been used to probe protein arrays. However, analysis tools to probe the spatial distribution of protein orientation and structure within individual spots on a microarray surface have not yet been developed. ***The availability of structure and chemistry sensitive imaging techniques is required to enable development of this next generation of biomedical arrays. The advances in NEXAFS and XPS based microscopic end-stations recently designed and implemented by the NIST Synchrotron Methods group hold great promise in this context.***

NEXAFS imaging allows macroscopic sample areas to be imaged with very high spectral quality, low X-ray exposure, virtually unlimited depth of focus and a spatial resolution of $50\ \mu\text{m}$. This makes the technique ideally suited for biological samples. NEXAFS imaging performed at NIST’s beamline U7A allowed us to create protein density and orientation maps of inkjet-printed bovine serum albumin (BSA) and RNase B arrays (Figure3).

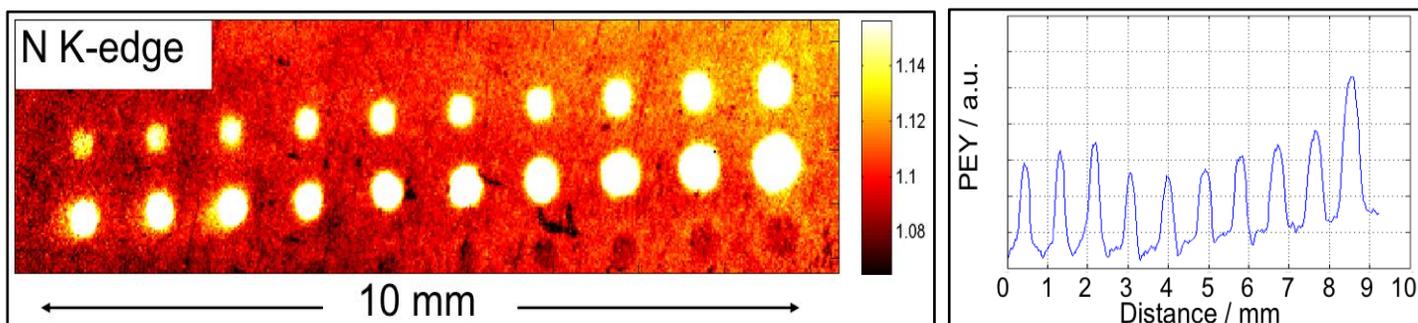


Figure 3: Left: Nitrogen K-edge image from NIST NEXAFS Microscope of a protein array printed onto a self-assembled monolayer. RNase (top row) and BSA (bottom row) are specifically bound via glycan linkers. Each pixel in the image contains a NEXAFS spectrum allowing orientation and chemical analysis. Right: Line analysis for the row of BSA spots. The intensity of the nitrogen signal varies with the protein surface density.

The *NIST XPS Microscope* (as designed for the NSLS-II) will have interesting applications towards the analysis of nanoparticles with biomedical coatings. Most specifically the depth selectivity (via variable photon energy from 100 eV to 7.5 keV) will be a significant advantage for analyzing the different layers of the nanoparticles. Current XPS techniques of angle resolved analysis to analyze layered materials are not applicable to nanoparticles. Thus, currently questions remain as to effectiveness of chemical modifications of the nanoparticle as well as where the chemical modifications are occurring (surface, sub-surface, bulk, etc.). NIST’s non-destructive depth analysis method that does not require a flat sample would add significant to this research.

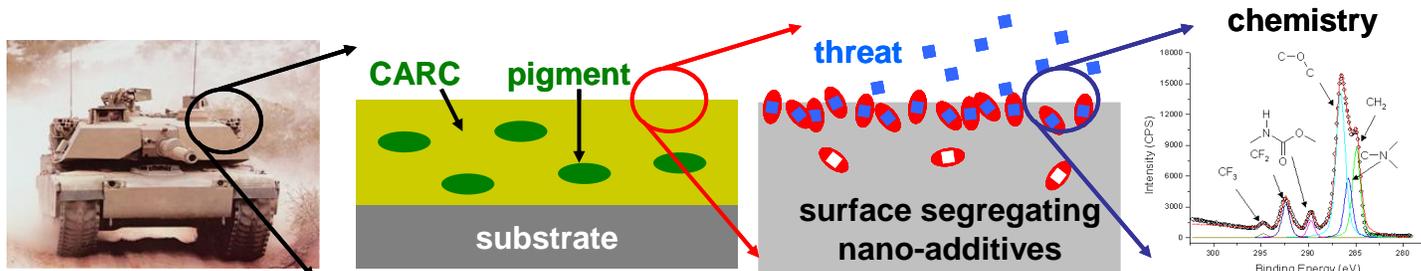
1. D. G. Castner and B. D. Ratner, *Surface Science*, 2002, 500 (1-3) , p 28.
2. T. A. Horbett, “Proteins at Interfaces – An Overview, in *Proteins At Interfaces*. 1995, ACS: Washington. P 1.
3. T. Weidner, J.S. Apte, L.J. Gamble and D.G. Castner, *Langmuir*, 2010, 25 (5) p 3433.
4. T. Weidner, N.T. Samuel, K. McCrea, L.J. Gamble, R.S. Ward, D.G. Castner, *Biointerphases*, 2010, 9 p 5.
5. J. E. Baio, T. Weidner, N. T. Samuel, K. McCrea, L. Baugh, P. S. Stayton D. G. Castner *JVST B*, accepted.
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Synchrotron Spectroscopy an Enabling Capability for the Defense and National Security Community

Joseph L. Lenhart (WMRD, US Army Research Laboratory)

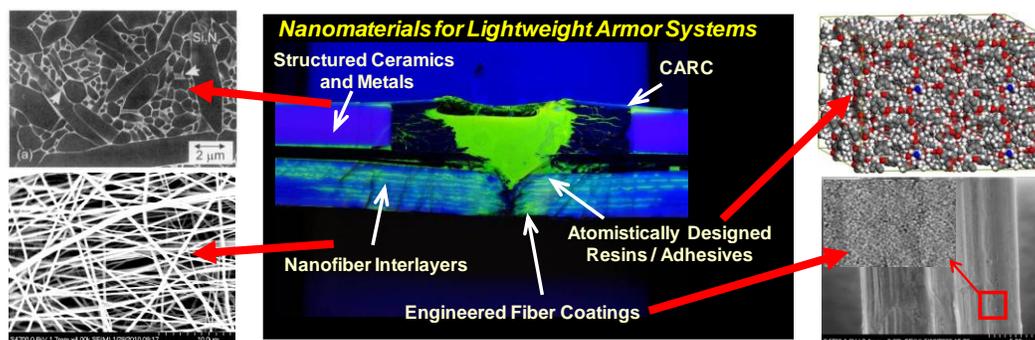
Current military drivers to reduce size, weight, power consumption, and cost; while still increasing performance; necessitate multi-functional materials with increased complexity.¹ Novel measurement techniques, with the capability to investigate the chemistry, structure, and properties in the bulk, at the surface at interfaces, and over various length-scales, with improved sensitivity, selectivity, spatial resolution, and through-put, are critical enablers of current and future national security missions. The Weapons and Materials Research Directorate (WMRD) at the US Army Research Laboratory executes fundamental and applied research programs involving polymer systems for military applications. Polymer based materials and devices are pervasive in the national security community with applications ranging from vehicles and armor to combat casualty care and first responder capabilities. *The following pages highlight two national security related research programs within WMRD, where the NIST proposed beamlines at the NSLSII can provide enabling measurement capabilities.*

Chemical and Biological Defense: Chemical and biological warfare and terrorism represents a substantial threat to both military personnel and civilians.² The Department of Defense currently protects its assets (tanks, vehicles, aircraft, etc) from chemical contamination by using CARCs (Chemical Agent Resistant Coatings).³ Future CARCs will be complicated polymeric systems that are deliberately engineered to degrade and prevent the permeability of a broad spectrum of chemical, biochemical, and environmental threats. Figure below shows a schematic of a future CARC. A polymer matrix provides the mechanical base. Pigments, as well as, micro and nano scale fillers will be added to control material properties. Active chemical receptors will be engineered to segregate to the film surface, both detecting and degrading a threat. Electronic circuitry will be integrated into the film to provide additional functionality.



The CARC surface represents an intelligently designed array of materials where various length-scales are critical: the macroscopic surface chemistry of the polymeric resin (mm or larger); the integrated electronics and pigment additives (10's of microns); the nano-fillers (10's nano-meters); the catalytic nano-additives that degrade the threat (10's nano-meters); the filler-resin interface (nano-meters); and the specific receptor sites for agent detection (angstroms). *The NIST beamline at NSLSII can facilitate future CARC development in the following manner:* 1) higher brightness and state of the art detector technology will provide improved peak resolution to extract the chemical details in these complicated formulations; 2) higher through put capability on the current U7A and X24A beamlines along with NEXAFS microscopy will provide rapid, combinatorial screening capability for optimizing the complex formulations; 3) the energy range from 100 to 7500 eV enables investigation of core level transitions for C, N, O, F, P, S, Cl, K, and Ca, all of which are important for the various materials, threats, and countermeasures that will be exploited in future CARC coatings; 4) the NEXAFS microscopy with micron resolution and XPS microscopy with nm scale resolution will allow chemical mapping of the surface over critical length scales enabling detailed investigation of threat adsorption, mobility, and degradation mechanisms on the CARC surface; 5) Variable Kinetic Energy XPS coupled with microscopy will enable investigation of compositional gradients at the film surface as a function of depth, which is critical for CARC effectiveness, since certain additives are engineered to segregate to the film surface.

Armor Systems: Light weight body and vehicle armor systems are critical for protecting soldiers, while enabling stealth and maneuverability. Figure below shows a model armor package composed of a metal or ceramic plate (top) adhered to a fiber reinforced polymer composite backing (bottom). The armor was shot by a high velocity projectile. Light green coloring highlights the damage zones. Similar to CARCs, future armor packages will be complicated materials systems with critical length scales ranging from angstroms to microns. The ceramic plates will have grain sizes from microns to tens of nanometers, and nano-scale grain boundaries that control energy absorption. The fiber reinforced polymer will have micron scale fibers with nano-fiber interlayer mats to control crack propagation. The micron scale fibers will have nano-roughened surfaces and atomistically engineered chemical coatings to enhance damping behavior and interfacial friction during fiber pull-out. The polymer resin will be engineered to optimize strength and energy dissipation, while containing nano-additives to further improve high strain rate toughness. Interfaces in these armor systems are critical for controlling functional properties.⁴ **However, no current techniques offer the chemical sensitivity or spatial resolution necessary to fully investigate these interfacial regions. In particular, the microscopy techniques developed at the proposed NIST beamline at NSLSII, will provide this measurement capability.** For example, the microscopy techniques will enable characterization of the nano-scale chemical heterogeneities on fiber coatings, and the nano-scale interfacial regions at a polymer-substrate interface, both of which are postulated to control composite performance.



The discussions above present two programs where interfacial phenomena dominate the system level response. **The advanced interfacial characterization equipment that will be developed for the NIST beamlines at NSLSII will provide the throughput, chemical sensitivity, and spatial resolution to intelligently design and optimize the critical interfacial regions in these systems. While the examples presented are defense related, advancement of these materials (facilitated by the NSLSII) will have a much broader societal impact.** For example, variations of CARC coatings are being explored as antimicrobial / antibacterial paints and coatings for construction materials, transportation facilities, clothing, and hospitals.⁵ They could be particularly beneficial for medical facilities in poverty stricken regions of the world, where the extensive cleanliness practices of today's modern hospitals are not affordable. The principles of high strength, light weight, and high toughness armor systems will be readily transferable to automobiles and commercial transportation enhancing the safety and fuel efficiency in this broad economic sectors.⁴

1. B. K. Fink, "Performance Metrics for Composite Integral Armor," *J. Thermoplastic Comp. Mater.*, **13**, 417, (2000).
2. Greenfield R. A., et. al., "Microbiological, Biological, and Chemical Weapons of Warfare and Terrorism," *Amer. J. Med. Sci.*, **323**, 326 (2002); Eubanks L. M., et. al., "Technological Advancements for the Detection of and Protection Against Biological and Chemical Warfare Agents," *Chem. Soc. Rev.*, **36**, 458 (2007).
3. K. R. Stone, D. A. Tolle, "Life Cycle Assessment of Chemical Agent Resistant Coatings" *Int. J. LCA*, **3**, 3 (1998); <http://www.ppg.com/corporate/governmentsolutions/militarydefense/MilitaryCoatings/Pages/topcoats.aspx>
4. P. J. Hogg, "Composites in Armor," *Science*, **314**, 1100 (2006); R. E. Jensen, S. H. McKnight, "Inorganic-Organic Fiber Sizings for Enhanced Energy Absorption in Glass Fiber Reinforced Composites Intended for Structural Applications," *Comp. Sci. Technol.*, **66**, 509 (2006).
5. L. Chen, et. al., "Multifunctional Electrospun Fabrics via Layer-by-Layer Electrostatic Assembly for Chemical and Biological Protection," *Chem. Mater.*, **22**, 1429 (2010).

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Nano to Microscale Spectroscopy for Environmentally Friendly Marine Anti-fouling Coatings

Edward Kramer (UCSB)



Figure 1 Fouling on ship in Gulf of Alaska – photo courtesy A. Hexemer.

considerable research effort is now focused on examining the potential of a range of antifouling surface designs that reduce the initial attachment of organisms.^{9,10} In the biomedical field, success in preventing biofouling has been achieved at the hydrophilic end of the wettability spectrum, for example, through the use of poly(ethylene glycol) (PEG) materials.¹¹ When PEG polymers are grafted to a surface, a close association exists between water molecules and PEG arising from hydrogen bonding. Such formation of a hydration layer has been shown to hinder the nonspecific adsorption of proteins¹² and has the potential to deter the adhesion of cells or microorganisms.¹³

Several studies on the settlement of marine algae have indicated a preference for hydrophobic compared to hydrophilic

The fouling of ship hulls and other man-made marine structures causes high operational and maintenance costs to industry (~ \$3 billion/yr) and increased carbon emissions (~20 million tons) across the world.⁷ An example of extreme fouling is shown in Figure 1. Traditional antifouling paints have relied upon the inclusion of biocides, most of which are now considered to be environmentally undesirable. In recent years, research has focused on the development of environmentally benign fouling-release coatings, especially low modulus, low surface energy silicone elastomers.⁸ Although these materials readily release most macrofouling organisms, they do not deter settlement or colonization, i.e., they are not “antifouling”. Therefore, a

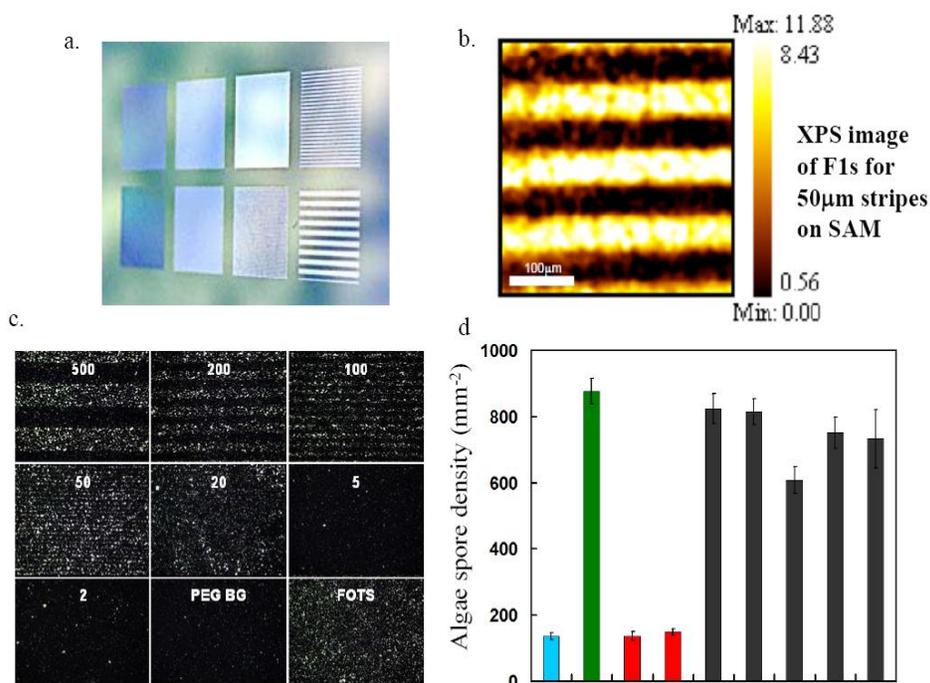


Figure 2 a.) Stripe patterns of perfluoroalkyl and PEG self-assembled monolayers on Si. b.) XPS image of photoelectrons from the F1s core level – the spatial resolution for this commercial instrument is ~ 5 μm. c.) Fluorescence optical microscopy images of *Ulva* spores on stripe patterns of various width (μm). d.) *Ulva* spore settlement on SAM patterns – note when the stripes are 5 μm or narrower, the settlement is greatly reduced.¹⁷

⁷ Townsin, R. L. *Biofouling* 2003, 19 (supplement), 9.

⁸ Brady, R. F.; Singer, I. L. *Biofouling* 2000, 15, 73.

⁹ Krishnan, S.; Wang, N.; Ober, C. K.; Finlay, J. A.; Callow, M. E.; Callow, J. A.; Hexemer, A.; Kramer, E. J.; Sohn, K. E.; Fischer, D. A. *Biomacromolecules* 2006, 7, 1449.

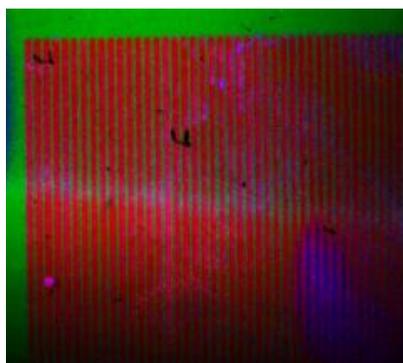
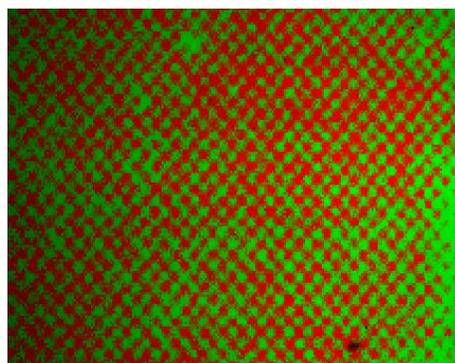
¹⁰ Genzer, J.; Efimenko, K. *Biofouling* 2006, 22, 339.

¹¹ Senaratne, W.; Andruzzi, L.; Ober, C. K. *Biomacromolecules* 2005, 6, 2427.

¹² Harder, P.; Grunze, M.; Dahint, R.; Whitesides, G. M.; Laibinis, P. E. *J. Phys. Chem. B* 1998, 102, 426.

¹³ Andruzzi, L.; Senaratne, W.; Hexemer, A.; Sheets, E. D.; Ilic, B.; Holowka, D.; Kramer, E. J.; Baird, B.; Ober, C. K. *Langmuir* 2005, 21, 2495.

surfaces.^{14,15} However, the strength of attachment of settled zoospores is typically stronger to hydrophilic compared to hydrophobic surfaces.¹⁶ These differences in settlement and adhesion behavior have inspired the development of “ambiguous” surfaces, which present both hydrophilic and hydrophobic domains to settling (attaching) cells and organisms. In recent years, a number of novel coatings in which the surface layers phase-segregate to produce a mosaic of hydrophilic and hydrophobic domains have shown promise as foul-release coatings.^{17,18} In the amphiphilic networks formed from hyperbranched fluoropolymer and linear poly(ethylene glycol), the dimensions of the surface-segregated components inferred from AFM images are in the micrometer range,¹¹ while the amphiphilic block copolymers of Krishnan et al.¹² may present a surface that is heterogeneous on a much finer length scale. The optimum design of “ambiguous” segregated surfaces requires information regarding the scale at which settling cells detect hydrophobic or hydrophilic domains. This has been explored through the use of patterned model surfaces, showing that when the hydrophobic/hydrophilic pattern was on a sufficiently small scale, algae cells do not settle (Figure 2).¹⁹



*NIST recently demonstrated a new, full-field NEXAFS microscope (at NIST’s U7A beamline) that is capable of measuring the patterned surfaces of figure 2. The images to the left are made using Principal Component Analysis of a NEXAFS image stack, green is FOTS and red is PEG SAMs with 100 micron features. **These NEXAFS prototype large area full field images***

*highlight the chemical bond sensitivity and selectivity of this new imaging method. At NSLS-II NIST will be extending this important capability to the micron scale. Patterned surfaces, with pattern dimensions comparable to those of cells and below, continue to be of interest in the study of cell-surface interaction in other contexts as well, for high-throughput screening, for example.¹⁴ A major unmet challenge however, especially for non-regular coatings, is to characterize the composition distribution over the ambiguous surface. **This is where the NIST SST NSLS-II Beamline Suite will have a major impact. Chemists and material scientists developing these coatings and patterned surfaces will have the capability to use NEXAFS in a way never before possible to microscopically image concentrations and orientations of organic groups down to length scales (~ 1 μm) never before possible. Depth profiling will be possible by using a unique, semicircular 33 electron detector array as well as by varying the negative bias grid voltage on the detectors. The soft and tender XPS microscopy capability of this Beamline Suite will likewise provide spatial resolution parallel to the surface to ~10 nm while state of the art XPS systems now struggle to achieve 5 μm resolution. Better still, the possibility for tuning the incident X-ray energy over the range from 100 eV to 7.5 keV will lead to a combination of depth resolution and depth penetration never before possible. Finally NEXAFS and XPS are almost completely complementary spectroscopies so having this combination of beamlines side by side will enable rapid and complete analysis of these chemically non-uniform surfaces.***

¹⁴ Ista, L. K.; Callow, M. E.; Finlay, J. A.; Coleman, S. E.; Nolasco, A. C.; Simons, R. H.; Callow, J. A.; Lopez, G. P. *Appl. Environ. Microbiol.* 2004, 70, 4151.

¹⁵ Statz, A.; Finlay, J.; Dalsin, J.; Callow, M.; Callow, J. A.; Messersmith, P. B.. *Biofouling* 2006, 22, 391.

¹⁶ Finlay, J. A.; Callow, M. E.; Ista, L. K.; Lopez, G. P.; Callow, J. A. *Integr. Comp. Biol.* 2002, 42, 1116.

¹⁷ Gudipati, C. S.; Finlay, J. A.; Callow, J. A.; Callow, M. E.; Wooley, K. L. *Langmuir* 2005, 21, 3044.

¹⁸ Krishnan, S.; Ayothi, R.; Hexemer, A.; Finlay, J. A.; Sohn, K. E.; Perry, R.; Ober, C. K.; Kramer, E. J.; Callow, M. E.; Callow, J. A.; Fischer, D. A. *Langmuir* 2006, 22, 5075.

¹⁹ Finley, J.A., Krishnan, S.; Callow, M.E.; Callow, J.A.; Dong, R.; Asgill, N.; Wong, K.; Kramer, E.J.; Ober, C.K. *Langmuir*, 2008, 24, 503.

Spectroscopy and Microscopy for Advanced Hard and Soft Materials: Energy and Microelectronics
Gary Mitchell (Dow Chemical Company)

The Dow Chemical Company is a chemical and advanced materials manufacturer. It connects chemistry and innovation with the principles of sustainability to help address many of the world's most challenging problems such as the need for clean water, renewable energy generation and conservation, and increasing agricultural productivity. Dow's diversified industry-leading portfolio of specialty chemical, advanced materials, agrosiences and plastics businesses delivers a broad range of technology-based products and solutions to customers in approximately 160 countries and in high growth sectors such as electronics, water, energy, coatings and agriculture. Dow R&D has been one of the top industrial users of synchrotron technology over the last 15 years.

The Dow Chemical Company has partnered with NIST to characterize advanced materials using x-ray spectroscopy techniques at the NSLS for over 14 years. Dow and NIST collaborated to build a materials science end station at U7A that has been continually updated by NIST and now provides a powerful arsenal of unique tools for characterization of both soft and hard materials with soft x-rays. We are eagerly looking forward to utilizing the NIST expanded capabilities that will be provided by the new NIST beamlines at NSLS-II and the new instruments that are being developed now for placement at NSLS-II. We are particularly excited about the new microscope capabilities being developed, but will still need access to the strictly spectroscopic probes as well.

Microscopy

In fabricating integrated circuits, photolithography technology is continually being advanced to keep up with the diminishing dimensions needed to make smaller, lower power consumption and faster electronics. Dow has active R&D programs in this area and has an ongoing need for analytical methods that can resolve features at ever decreasing size scales and provide chemical details necessary for progress. For instance, we have used scanning photoemission micro-spectroscopy (SPEM) for analyzing features in circuits made with Photo-BCB (CYCLOTENE™ 4024 or 4026 Advanced Electronics Resins) which are photosensitive polymers developed by The Dow Chemical Company for use in micro-electronics applications [20]. One important issue to understand is how fully the polymer is removed from the surface in unexposed areas during developing. The material left in unexposed areas after developing has been called “scum” and procedures to “descum” these areas by plasma cleaning have been developed, but it is difficult to determine the quality of the descumming in a precise sense, due to the spatial limitation of the laboratory based XPS measurements. (Electron microscopy only helps here when scum is many molecule layers thick.) Using the SPEM we were able to image patterned surfaces and from microprobe spectra, calculate the relative

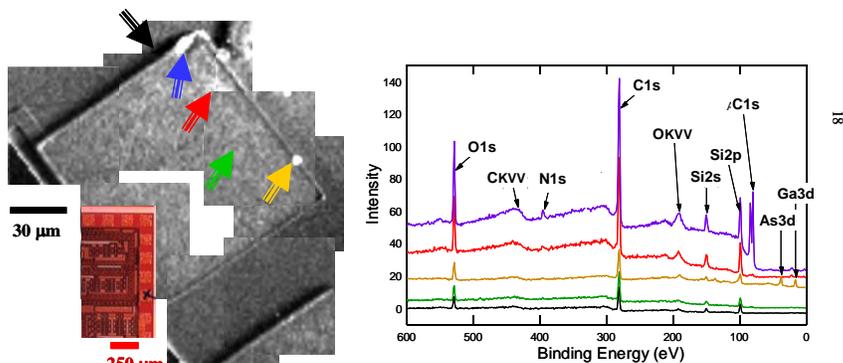


Figure 2. A montage of SPEM images which together provide an image of most of a large gold solder pad located near the edge of the die. At bottom left is a visible light microscope image of the die. The x marks the gold solder pad imaged by SPEM. The differently colored arrows indicate where the microprobe XPS spectra in the graph at right were obtained.

²⁰. E. Rutter jr., E. Moyer, R. Harris, D. Frye, V. St. Jeor, and F. Oaks, Proceedings of First International Conference on Multichip Modules (ISHM & IEPS), Denver Co, (1992) 394.

surface coverage of contaminants and thus determine the quality of descumming procedures (Figure 1) [21]. However the SPEM measurements are limited by electrical surface charging [2]. ***The new technology being developed by NIST will allow the use of charge compensation methods that are already well developed for lab based instruments to compensate charging and provide good quality data even for insulator surfaces. Photoemission electron microscopy (PEEM) also suffers from charging issues that prevents its use for surfaces of insulators and many materials questions that have been solved with PEEM, such as mono or few layer wetting-dewetting phenomena [22] will be applicable to insulator surfaces using the NIST XPS microscope.***

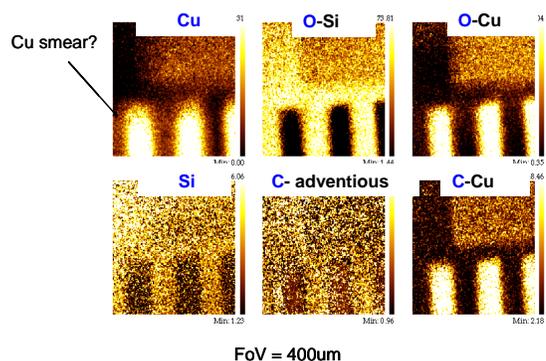


Figure 3. XPS images of a Si based IC with Cu connectors. The quantified images are generated by collecting a hyperspectral image and deconvolving into elemental images.

A critical issue to Dow's program in advanced electronic materials is to determine the quality of surfaces of integrated circuits after undergoing planarization using chemical mechanical polishing (CMP) to understand smearing of phases. This is a breakthrough technology that has been developed in the last few years and has revolutionized IC manufacturer. By using CMP in between layers of an IC, many more layers are now possible on a single device, increasing the allowed complexity. This is one of the key enablers for the dual and larger microprocessors, for instance. The spectral images reproduced in Figure 2 were measured on our lab based XPS system with 30 μm spatial resolution. ***The spatial resolution of the NIST XPS microscope will be applicable to many more situations with transistor dimensions smaller than 100 nm and by varying the excitation energy one will be able to quantitatively measure thicknesses.***

Spectroscopy

An important area of research at Dow involves developing new catalyst systems and enhancing existing ones to manufacture products more efficiently and with fewer byproducts to minimize waste. These catalyst systems are often heterogeneous, meaning they consist of a solid catalyst interacting with a fluid phase reactant stream. The solid catalyst usually is some active metal species supported on a ceramic carrier that provides a high surface area to increase contact with the gas or liquid reactants and products. In order to understand the microscopic details of the reactions that take place on a catalyst we have partnered with NIST to use the unique Multi-Layer-Mirror (MLM) facility at U7A to analyze catalyst being developed. ***With MLM one can detect very low levels of carbon or nitrogen based intermediates adsorbed on a catalyst with reactant gases present using fluorescence yield near edge x-ray absorption [23].*** Usually the presence of reactant gases and the high level of oxygen in the support would obscure the signal coming from the low level of adsorbed intermediates on the catalyst. The MLM is tuned to the C (or N) fluorescence only, thus providing sufficient signal to detect the adsorbed species [24]. The MLM was used to study an experimental catalyst being developed to make propylene oxide by a direct pathway from oxygen and ethylene without need for chlorinated intermediates [3]. Propylene oxide is one of the highest volume chemicals made in the world and is used in the production of plastics, surfactants and non-toxic antifreeze, so that limiting byproducts and maximizing the efficiency of conversion is important to the world environment and economy. Using the MLM instrument, one can observe

²¹. Gary E. Mitchell, Dan Scheck, Dave D. Hawn, Greg F. Meyers, Ralf Graupner, George Meigs, Ivaylo Koprinarov, ALS Compendium of User Abstracts 2000.

²². David Tulumello, Glyn Cooper, Ivo Koprinarov, and Adam P. Hitchcock, Edward G. Rightor, Gary E. Mitchell, Steve Rozeveld, Greg F. Meyers, and Ted M. Stokich, J. Phys. Chem. B 2005, 109, 6343.

²³. S. Sambasivan, D. A. Fischer, A. Kuperman, B. M. DeKoven, Adv. Mater. 2000, 12, 1809.

²⁴. D. A. Fischer, S. Sambasivan, A. Kuperman, Y. Platonov, J. L. Wood, Rev. Sci. Instrum. 2002, 73, 1469.

the chemical state of adsorbed propylene inside the cavities of a zeolite (which was the porous, high surface area ceramic support in this case) and assess the degree of perturbation to the double bond which is related to the ease of reaction with the oxygen to form the product propylene oxide. ***This MLM technology will be even more powerful on NSLS-II with the higher intensity available there.***

Other areas where the NIST spectroscopic probes proposed in this beamline proposal will be key to breakthroughs in understanding materials and driving progress include characterizing surfaces and thin films for photovoltaic devices, advanced battery materials such as high performance cathodes, separators and anodes, improved reverse osmosis membranes, functional coatings and buried interfaces in complex materials. NIST's proposal highlights the use of variable excitation energy XPS one can non-destructively profile the chemistry as a function of depth up to about 25 nm at 7.5 keV [25]. This technology has been shown to be useful in understanding and optimizing the phase structure of thin film solar cells [25] and with charge compensation, it will be very useful to understand films on insulating polymeric materials.

Reverse osmosis membranes have shown improvements in their properties (resistance to fouling, enhanced salt rejection or flux) by coating the surface of the discrimination layer with various chemistries [26,27, 28, 29]. The surfaces of RO membranes, especially, of the FT30 type with polyamide discrimination layer are very rough [28] and thus depth profiling by angle resolved XPS or sputter depth profiling XPS give inaccurate results.

In order to analyze the chemistry and depth of coatings, NIST's variable excitation XPS will be more accurate. Nanoscale imaging capability will allow the determination of lateral uniformity as well. The in-situ NEXAFS capabilities at U7A have already been shown to be useful for analysis of Li ion batteries [30]. Dow has recently announced that it is investing in a new plant to make Li ion batteries for use in electric automobiles [31]. In-situ characterization of batteries using the NIST beamlines is expected to provide very useful information about chemical and structural changes occurring during charging and discharging. The important issues to resolve with these sorts of batteries involve the loss of capacity with cycling and increasing the power to weight ratio. The loss of capacity may be related to chemical structure changes that occur in the cathode during charge-up. The metals in the cathode and anode, as well as C based species in the electrolyte are all possible to analyze by L-edge or K edge x-ray absorption spectroscopy with soft or tender x-rays. The L-edge spectroscopy of transition metals which make up the cathode intercalation compounds is particularly sensitive to the valence electronic structure [32, 33]. By measuring the chemical structure in-situ at different charge states and after varied amounts of cycling we hope to understand and improve capacity reduction caused by cycling.

²⁵. H. Mönig, Ch.-H. Fischer, R. Caballero, C.A. Kaufmann, N. Allsop, M. Gorgoi, R. Klenk, H.-W. Schock, S. Lehmann, M.C. Lux-Steiner, I. Lauermaun, Acta Materialia 57 (2009) 3645.

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³¹. http://www.mlive.com/business/mid-michigan/index.ssf/2009/04/dow_chemical_battery_venture_w.html.

³². J. G. Chen B. Frühberger, and M. L. Colaianni, J. Vac. Sci. Technol. A 14(1999) 1668.

³³. Shirakawa J, Nakayama M, Wakihara M, et al., J. Phy. Chem. B, 110 (2006) 17743.

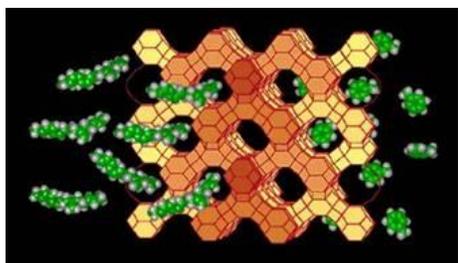
Advanced Spectroscopy Promoting Breakthrough Catalysts for Energy Applications

Simon R. Bare (UOP LLC, a Honeywell Company)

UOP LLC, headquartered in Des Plaines, IL, USA, is a leading international supplier and licensor of process technology, catalysts, adsorbents, process plants and consulting services to the petroleum refining, petrochemical, and gas processing industries. UOP is a wholly-owned subsidiary of Honeywell International, Inc. and is part of Honeywell's Specialty Materials strategic business group. UOP has been using synchrotron radiation primarily to probe the structure of its catalysts and adsorbents since the early 1980's and was a charter member of the original Matrix PRT at the NSLS in the mid-1980's. UOP is currently a member of MR-CAT at the APS and a member of the SCC at the NSLS and has collaborated with NIST at the NSLS for many years. ***This collaboration is essential; we anticipate full utilization of the world-class capabilities of SST.***

UOP fully supports the development and construction of the SST beamline suite by NIST. The capabilities envisioned for this suite of beamlines are unparalleled, and will provide new insights into catalyst structure and function leading to development and implementation of new breakthrough catalyst systems. In this section, due to space limitations, only a single catalyst system is discussed: zeolitic catalysts. However, this example shows how the complementarity of the techniques proposed at SST will beautifully combine to provide a complete picture of the characterization of this important class of catalyst.

The use of zeolites and molecular sieves in catalysis and adsorbent technology is ubiquitous³⁴. The annual market is estimated to exceed 1.8 million tons worldwide, and have applications ranging from petroleum refining to use in detergents to nuclear waste cleanup. There is an ever increasing discovery of new compositions and structural topologies. Basically zeolites and molecular sieves are solids with pores of the size of molecular dimensions. One traditional class of these materials is known as aluminosilicates, and is comprised of infinitely extending 3D four-connected framework of AlO_4 and SiO_4 tetrahedra. The substitution of aluminum (+3 cation) into the silicate (+4 cation) framework leads to the presence of Brønsted acid sites. It is this acidity which leads to an



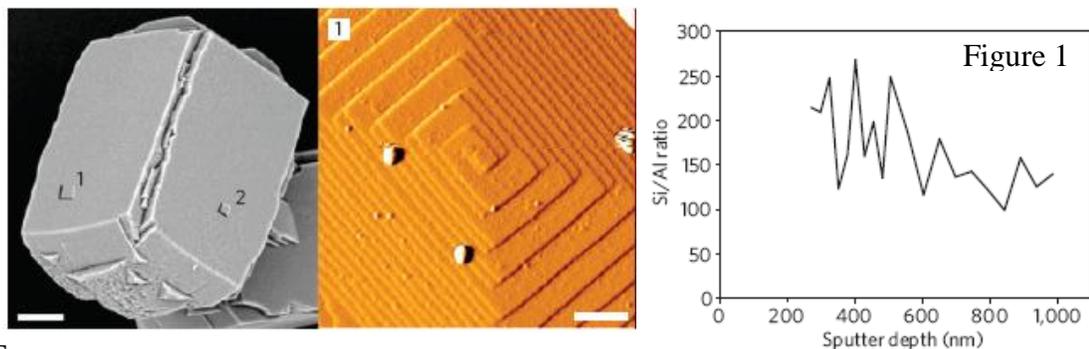
important application of these materials: as a solid acid catalyst. The exact location, and acid strength, and subsequent activity of these acid sites in the often complex zeolite framework is of ongoing research. Moreover, in the commercialization of a zeolite the material may undergo numerous post-synthesis treatments to stabilize and modify the activity. Each of these treatments will affect the activity of the zeolite, and potentially change the morphology and location and distribution of the aluminum. These treatments include calcination, steaming, acid washing, and surface modification. There are a plethora of catalyst characterization techniques that can be used to characterize catalysts, each with particular strengths and weaknesses. ***The suite of characterization capabilities at SST will open up a new regime for zeolite characterization from micro to nano length scales.***

For example, pore mouth catalysis has long-been debated in the literature³⁵. This has huge implication for the processing of heavy petroleum feeds where the molecules may be too large to enter the pores, or for processing feeds of mixed molecular weight where one reactant may diffuse into the zeolite and another may not. The key question here is the location of the acid sites in the zeolite crystal and whether there is a gradient of aluminum in the zeolite. This is even more relevant as new synthesis methodologies are developed to produce nano-size zeolite particles. XPS has been the technique of choice for determining the Si/Al ratio in a zeolite, but due to the high mean free path of photoelectrons using a laboratory XPS instrument the signal originates from the outer 4-10 nm - thus not truly surface sensitive. ***The variable kinetic energy XPS (VKE-XPS) beamline pair (100 eV to 7.5 keV) proposed in SST will allow, for the first time, non-destructive depth profiling from the outer surface***

³⁴ Zeolites in Industrial Separation and Catalysis, Wiley-VCH, Weinheim, Germany, 2010. S Kulprathipanja, Ed.

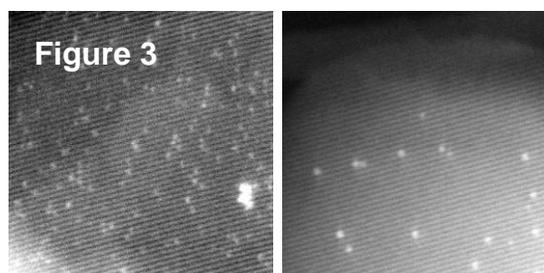
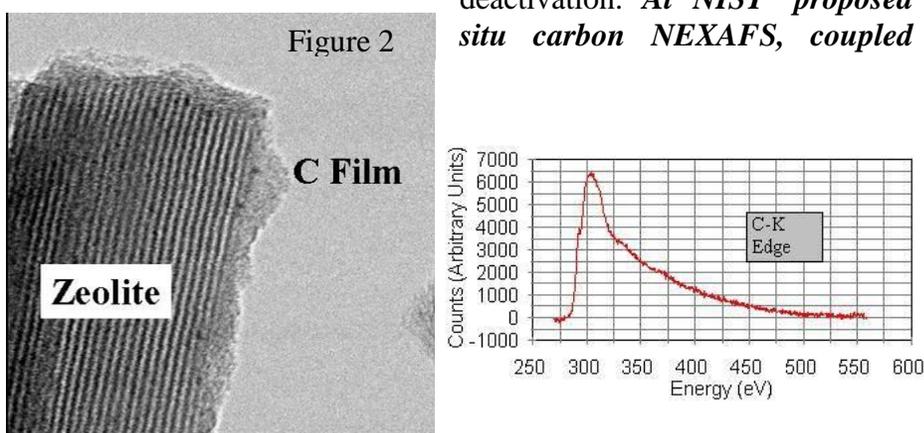
³⁵ P.C. Mihindou-Koumba et al., J. Catal. 255 (2008) 324; J.A. Martens et al., Angew Chem. Int. Ed. 107 (1995) 2726; W. Souverijns et al., J. Catal. 174 (1988) 177.

layer to deep into the bulk of zeolites. Thus, this critically important information will be obtained as a function of the calcination temperature/time, steaming temperature/time, etc. for a wide array of zeolite topologies. **An intriguing extension of this is to determine this information from individual zeolite crystals by making use of the NIST's proposed XPS microscope and variable VKE.** Outer surface molecular diffusional barriers have recently been identified in zeolite intergrowths, but the supporting XPS data were collected using a laboratory instrument drastically limiting the information content as the Si/Al ratio were obtained destructively used sputter depth profiling. Figure 1 shows the SEM, AFM and XPS-derived Si/Al ratio as a function of sputter depth of a single MFI zeolite crystal³⁶.



As zeolites are used in hydrocarbon processing they often deactivate with time on stream. Identifying the cause of the deactivation is often not straightforward. example Figure 2

For shows the bright field TEM image of a carbonaceous residue on a spent zeolite together with the carbon K-edge EELS spectrum (below) from the film showing the carbon to be primarily amorphous. It was believed that the buildup of this carbon led to the **SST using the capabilities of the in with the VKE-XPS we will be able to study the structure of the carbon in the initial stages of the reaction - something that cannot be studies in the TEM.** Carbon NEXAFS is ideal tool for studying these deposits: it has high sensitivity, the total amount of C can be quantified, the type of carbon can be identified, surface and bulk signals obtained, and this work will be coupled with in situ studies.



Metals are often added to zeolites to provide bifunctional activity: the acid catalysis from the zeolite and the metal-catalysis from the added metal. For example, Figure 3 shows TEM images of Pt clusters inside a Y-zeolite. Here the growth of the clusters from 1 nm (left) to 2nm (right) from fresh to spent catalyst is clearly observed. The TEM can only show the size and shape of these Pt nanoclusters but reveals nothing about their catalytic activity. **The full suite of tools at SST will be used to provide catalytic activity in**

an unprecedented manner. The electronic structure of the Pt nanoparticles will be probed using the XPS microscope at nanometer length scales; using the adsorption of probe molecules (e.g. CO) carbon NEXAFS will provide information on the cluster size and shape and potentially location (internal or external to the zeolite); and the VKE-PE will provide non-destructive information on the depth distribution. Each will be conducted as a function of processing of the particular catalyst.

³⁶ L. Karwacki et al., Nature Mater. 8 (2009) 959.

Materials Research for Next Generation Lithium Batteries Using Soft and Tender X-ray Spectroscopy and Microscopy

Xiao-Qing Yang and Kyung-Wan Nam (Battery research group, BNL chemistry)

Batteries are the key elements of clean energy technologies for hybrid & electric vehicles (HEV & EV), smart grid to utilize the green energy sources such as wind and solar electric energies. The in-depth understanding of the changes in electronic and crystal structures of the electrode materials during charge-discharge cycling or under abuse conditions will provide the important information for developing new materials with higher energy and power densities, longer life and better safety characteristics. In this regard, the BNL battery research group has been carrying out DOE funded projects (Vehicle Technologies (VT) program, office of Energy Efficiency and Renewable Energy (EERE)) which focus on developing new diagnostic tools during charge-discharge cycling or under abuse conditions using synchrotron based hard and soft X-ray techniques. The primary objectives of these projects are to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity, power decline, and safety. To this end, the *BNL battery group has engaged in collaboration with the NIST Synchrotron Methods Group stationed at the NSLS and has conducted state of the art battery research using NIST's soft X-ray spectroscopy for more than 10 years. Soft X-ray absorption spectroscopy (XAS) at NIST beamline U7A has been unique diagnostic tools for our battery research.* For example, soft X-ray absorption spectroscopy (XAS) at NIST U7A beamline has been used to distinguish the structural differences between surface and bulk of cathode materials such as LiCoO_2 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ at certain states of charge-discharge

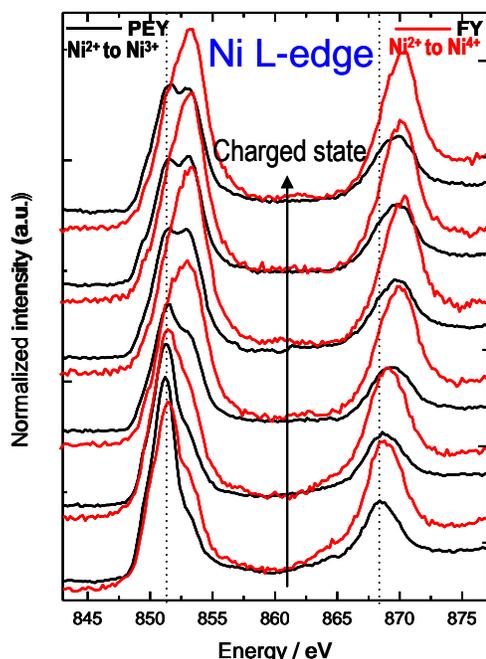
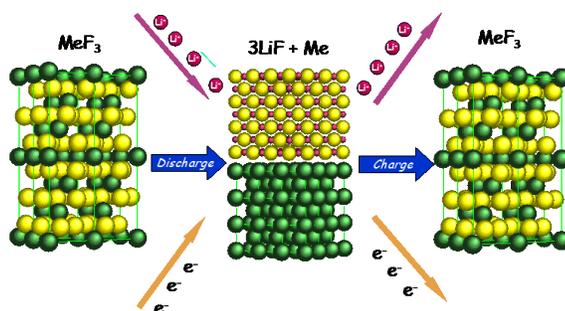


Figure 1. Ni L-edge NEXAFS spectra for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material during charge showing different electronic structure changes between bulk and surface.

using both electron yield (EY) and fluorescence yield (FY) detectors in both O-K and transition metal (Mn, Fe, Co and Ni) L-II, III edges.^{1,2} (Fig. 1) These results provided valuable information for the development of new battery materials with high capacity and the improvement in capacity of the materials being used currently. *Furthermore, These results demonstrate that the NIST's proposed NEXAFS/XPS beamlines are crucial and essential diagnostic tools for characterizing advanced battery materials.*

Reversible conversion nano-materials are new type of lithium battery materials which shows much higher specific capacity with 260% over today's state-of-the-art LiCoO_2 positive electrode material. Unlike the intercalation cathode materials like LiCoO_2 , reversible conversion process results in the full reduction of the transition metal cation to its elemental (i.e., metallic) state during the discharge.

(Scheme at right) However, although promising from a number of fundamental energy

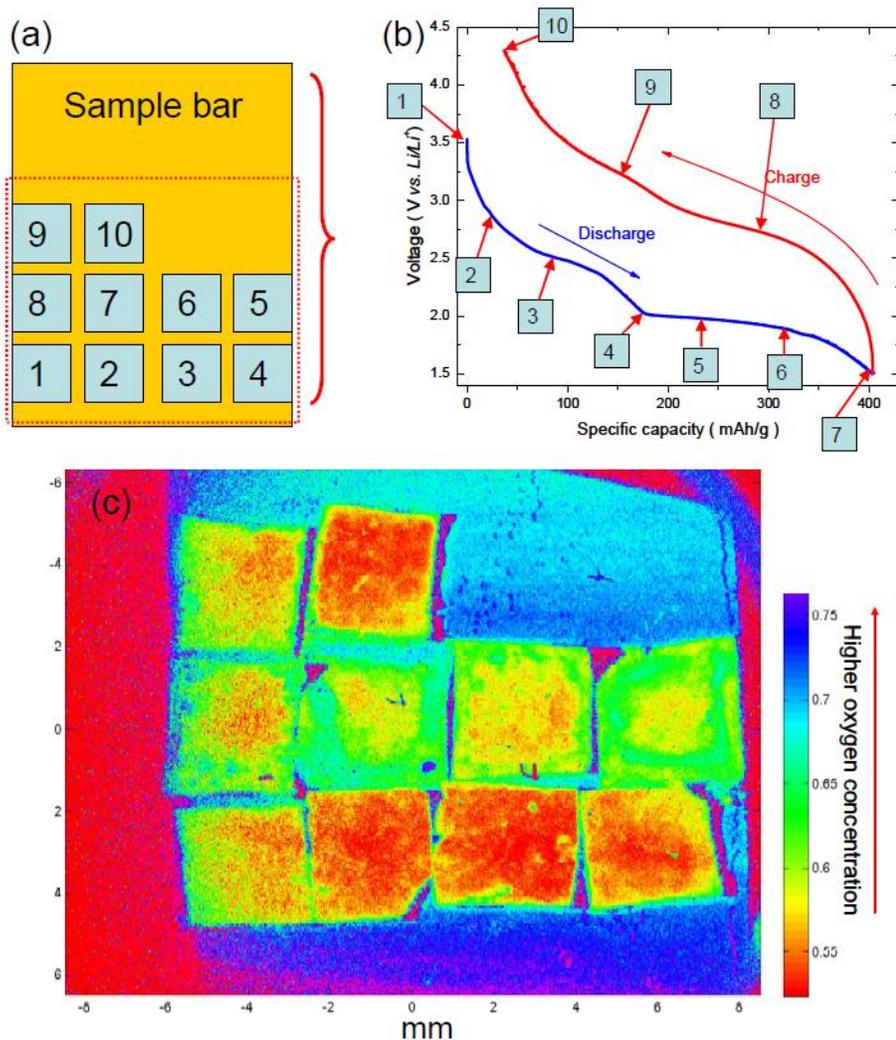


Schematic diagrams of conversion reactions used for energy storage materials.

perspectives, the conversion materials still face cycle life challenges and overpotentials in the voltage profile which decrease charge/discharge efficiency. In order to overcome above challenges, it is crucial to understand conversion/reconversion reaction pathways, and chemical/compositional perturbations induced during the charge-discharge cycles. In this regard, we have done NEXAFS microscope studies on a combinatorial array of FeOF nanocomposite electrodes with different state of charge-discharge at NIST U7A beamline. (Figure 2) The preliminary results are quite exciting and encouraging. As

sown in Fig. 2, we have clearly observed the reversible oxygen composition changes during the first discharge-charge cycle suggesting that the fluorine (F) is being extracted from and re-inserted to the FeOF nanocomposite materials during the conversion and reconversion reactions. In addition, NEXAFS image results provide spatial profiles about oxygen concentrations within each electrode. Regardless of the state of charge, relatively higher oxygen concentrations are observed especially at the edges of the rectangular shaped electrodes indicating the conversion reaction begins first at the edge sides.

Another critical question to be answered to the success of the conversion reaction approach is the elucidation on the formation of a locally stoichiometric, highly chemically-heterogeneous metal particle- Li salt nanocomposite on the order of 1-5nm during charge-discharge. The proposed NIST XPS microscope with nano scale spatial resolution will be ideal tool to characterize the nano-scale interface formed during conversion reaction. *Therefore, combination of NIST's proposed NEXAFS and XPS image microscopes with nano and micro scales will have enormous impact on the development of new advanced next-generation battery materials which are driven by displacement and conversion reactions.*



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Figure 2. NEXAFS microscope image results for combinatorial array of FeOF nanocomposite electrodes with different state of charge-discharge. (a) sample description; (b) charge-discharge curves of FeOF nanocomposite electrode; (c) oxygen K-edge NEXAFS mapping results.

Hard X-ray Photoelectron Spectroscopy (HAXPES) and Near Edge X-ray Absorption Fine Structure (NEXAFS) of Phase Change Materials for Next-Generation Non-Volatile Memory Applications
Eric A. Joseph and Jean Jordan-Sweet (IBM T.J. Watson Research Center)

Chalcogenide glass materials have recently garnered significant interest for solid-state, non-volatile phase-change memory (PCM) applications due to their potential for scalability beyond that of conventional DRAM and Flash memory technologies [1]. Additionally, such materials may serve in storage class memory (SCM) devices which would substantially reduce the number of devices, physical space, and power requirements necessary for Exascale Computing, enabling an energy efficient, green technology [2].

	2020 Storage Bandwidth Requirement		Disk	PCM SCM
Compute-centric	1.7 PB/s	Devices	5.6M disks	1.7M modules
		Space	26,292 sq.ft.	300 sq.ft.
		Power	25 MW	173 KW
Data-centric	8.4 Giga-SIO/s	Devices	21M disks	35,000 modules
		Space	98,568 sq.ft.	12 sq.ft.
		Power	93 MW	4 KW

Figure 1: Projected PCM Impact to Exascale Computing for compute-centric (Petabytes per second) and data-centric (Giga-start input outputs per second) applications [2].

Chalcogenide phase-change memory is based on the orders-of-magnitude change in resistivity these materials exhibit during rapid crystallization and re-amorphization. However, such device applications require specific crystallization properties to ensure that their crystallization temperature (Tx) is sufficiently above standard CMOS device operation ranges (~80°C), but also well below the melting point for thermal stability. Consequently, a thorough understanding of the phase-change material system and the role by which the material stoichiometry and local bonding environment affect the crystallization properties are important elements to optimizing the technology. As an example, one method of adjusting material properties is to dope the chalcogenide. Doping favorably modifies crystallization speed, crystallization temperature, and thermal stability. However, the chemical role of the dopant is not always understood, and in many cases it may lead to adverse effects.

IBM began collaborating with NIST in 2008 conducting state of the art, synchrotron research on chalcogenide material systems using the current NIST suite of spectroscopy beamlines at NSLS. The goal of the research was to provide a greater understanding of the local bonding environment of the material system and determine the specific location and bonding nature of the dopant atoms. An example of previous work is the high-energy XAFS measurements of nitrogen doped Ge₂Sb₂Te₅ completed on NIST beamline X23A2. By studying the Ge K edge, this work found that nitrogen doping preferentially forms stable Ge-N bonds. This result suggests that nitrogen doping does not lead to substitution of N into the FCC lattice, nor does it lead to distortion of the FCC lattice, but rather the N dopant instead resides on the grain boundary, where stability and structural nature of Ge-N and Ge-N-Ge bonding refines the grain [3].

It is eagerly anticipated that the electronic structure and local bonding geometry of the lighter “Z” dopant will be determined directly using Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) and high energy XPS at the new NIST NSLS-II soft and tender beamline. Under current conditions at NSLS, it was not possible to acquire such data from this sample (at NIST beamline U7A) due to the low level

concentration of the dopant. *The significantly higher brightness of the NIST NSLS-II Soft and Tender beamline and its advanced detector capabilities should allow such NEXAFS measurements of low level, low “Z” dopants. In addition, the beamline’s expanded energy range (100eV to 7.5 keV) and enhanced nanometer scale spatial resolution thanks to its ensemble of microscopes will enable chemical mapping of samples which have undergone various (re)crystallization treatments.*

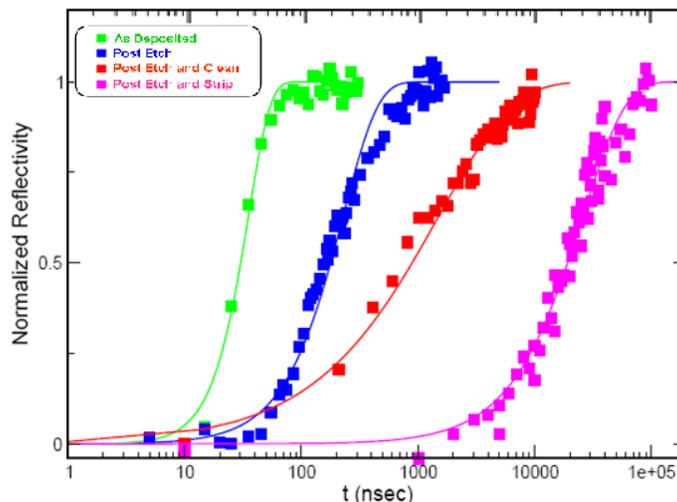


Figure 2: Normalized time resolved laser reflectivity measurements for as-deposited, plasma etched, plasma etched and cleaned and plasma etched and stripped nitrogen doped GeSbTe samples.

In addition to dopant specific studies, the effects of processing on the material crystallization properties are also of interest since it is known that there is an etch-induced material modification layer resulting from patterning [4]. Processing of chalcogenides significantly reduces their crystallization properties. Time resolved laser reflectivity data is shown in Figure 2, demonstrating a three order of magnitude shift in crystallization time upon exposure to the plasma etch and strip processes. To elucidate the nature of this material modification, a combination of depth profiled XPS, time resolved XRD, and XAS would be ideal. Results of previous depth profiled XPS data shown in Figure 3 obtained on a Physical Electronics Quantum 2000 ESCA Microprobe using a monochromatic Al K_{α} source reveal selective antimony removal and nitrogen dopant loss at depths up to 12nm. However, *such depth profiling measurements are extremely destructive in nature due to the use of 1.0 keV Ar+ ion sputtering which can cause significant disruption to the material itself.* In reality, the etch process likely created the non-uniform concentration of antimony and nitrogen that are measured for the amorphous control sample.

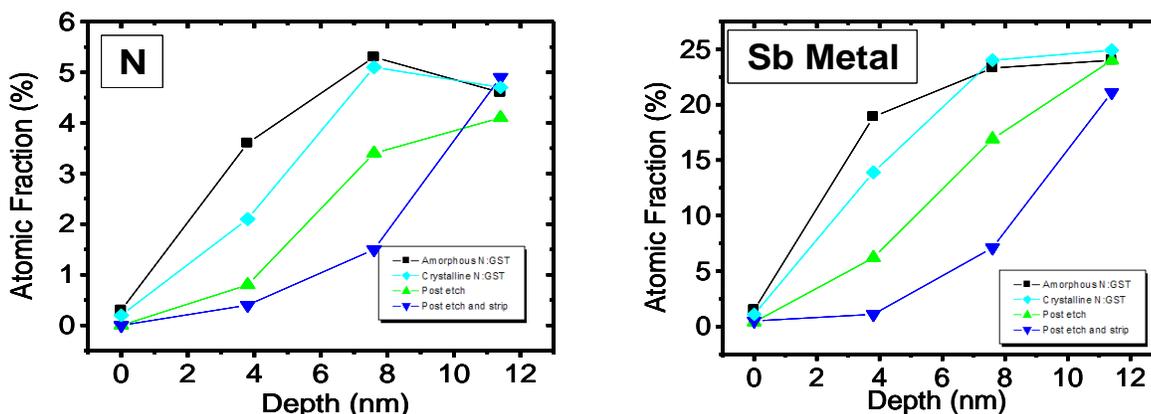


Figure 3: Depth profiled XPS measurements for N and Sb elements of N-GST films. Post-etch data follows etching in an Ar/CHF₃/Cl₂ chemistry. Post etch and strip follows the same etch with an additional dry strip [2].

As a big step towards alleviating this issue, variable kinetic energy XPS (VKE-XPS or HAXPES) obtained by varying the *incident photon energy* in a high resolution, high energy XPS measurement, a capability planned for the NIST NSLS-II Soft and Tender beamline, will provide non-destructive, depth profiling measurements simply by tuning the kinetic energy of the materials' core lines and exploiting the intrinsic, energy dependent, surface sensitivity of photoemission. This advancement should enable higher resolution, *non-destructive* and *unambiguous* depth profiling measurements for materials systems such as these. ***Coupled with the new nanometer scale spatial resolution planned for the VKE-XPS endstation, these advanced capabilities will effectively enable a 3D chemical imaging XPS microscope unique to NSLS-II.***

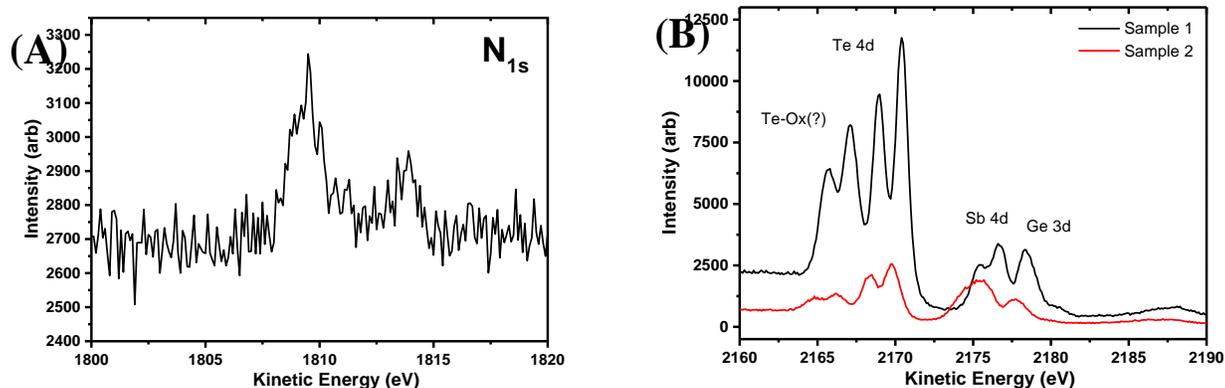


Figure 4: Synchrotron based XPS measurements of (A) nitrogen and (B) Ge, Sb, and Te core levels in N doped GST films measured with a photon energy of 2.1keV at NIST beamline X24A at the NSLS.

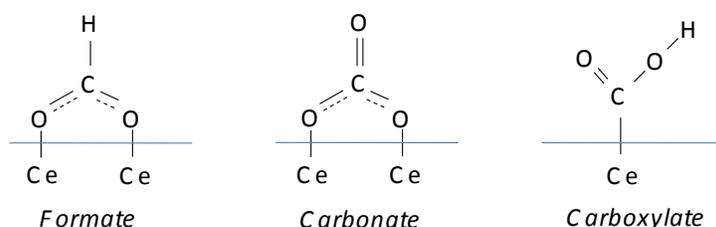
Already under development by the NIST team at NSLS, VKE-XPS (or HAXPES) data from NIST beamline X24 are shown in Figure 4. The data show the improved capability over a laboratory source to achieve high resolution XPS measurements for the N_{1s} core level in N-doped GST (Figure 3a) and the often elusive lower binding energy (BE=30-40eV) GST peaks such as Te_{4d}, Sb_{4d}, and Ge_{3d} core levels (Figure 3b). ***The benefit from higher flux VKE-XPS measurements available at NSLS-II will improve the signal to noise ratio of these data while providing the necessary depth and spatial resolution to generate an effective 3D chemical map.***

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**Fundamental spectroscopy studies of the active sites of metal/oxide catalysts:
Water-gas shift reaction on Au-CeO₂ and Cu-CeO₂ systems**
Jose A. Rodriguez, Chemistry Department, Brookhaven National Laboratory

The concept of the “active site” in catalysis has been used since its introduction in the 1920s by Taylor and Langmuir. However, despite considerable scientific effort over many years, our knowledge of what exactly the active sites are and how they really work is in most cases very primitive. It is necessary to identify the active site and fully characterize its electronic, structural and temporal properties, and their dependence on temperature. **What we propose here is a unique effort that will take advantage of the capabilities of NIST's Soft and Tender beamline for surface and materials characterization.**

With the onset of the hydrogen economy and future global energy challenges, the ability to produce molecular H₂ from a sustainable source has been pushed to the forefront of chemical research.³⁷ The water gas shift (WGS, CO + H₂O → H₂ + CO₂) in particular has come to the fore of catalytic reactions that can answer this problem, in particular with the ability to undertake this process with the use of relatively abundant resources (CO and H₂O). New ceria (Au, Cu or Pt on CeO₂) based nanocatalysts are very promising candidates for high activity, lower temperature WGS systems.^{38,39} These metal/oxide catalysts exhibit a substantially higher activity than the traditional Cu/ZnO WGS catalysts. The design and optimization of the ceria-based WGS catalysts is hindered by controversy about basic questions regarding the nature of the active sites and the reaction mechanism. It has been proposed with some controversy that the predominant intermediate species for this reaction is either a *formate* (HCOO⁻) or a *carbonate* (CO₃²⁻) and most recently theoretical calculations suggest the possibility of a *carboxyl* (HOCO⁻) intermediate:



Using the new capabilities of NIST's NSLS-II beamline, one will be able to study the kinetics of decomposition of *formate* and *carbonate* on different metal oxide surfaces and compare it with the overall rate for the formation of H₂ and CO₂ during the WGS reaction. This will point to the key intermediate as a function of surface composition. It has been observed that the *formate* and the *carbonate* have similar C 1s XPS signatures. **Since the NIST NSLS-II beamline will allow the combination of photoemission and NEXAFS studies,** it will be possible to distinguish the formation of *formate* or *carbonate* intermediates as a consequence of the reaction of CO and OH in the early stages of the WGS.⁴⁰ The characteristics of the beamline will make it an excellent tool for identifying active sites and for studying their behavior.

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²¹ Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, Science, 301 (2003) 935.

³⁹ J.A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, and M. Perez, Science, 318 (2007) 1757.

⁴⁰ S.D. Senanayake, D.R. Mullins, J. Phys. Chem. C 112 (2008) 9744.

**Optimizing Novel Materials for Energy Applications:
Electronic Structure of Doped Oxides Using Hard X-ray Photoelectron Spectroscopy (HAXPES)
Abdul Rumaiz (BNL)**

The finite nature of fossil fuels has created a greater need for an alternate and stable energy source. A significant portion of this effort has been directed towards solar energy and hydrogen generation. In both these areas there is a greater need for novel materials which can be tailored for higher efficiencies. Transitional metal oxides, especially titanium dioxide (TiO_2) and zinc oxide (ZnO), are being aggressively studied as viable photovoltaics and photocatalysts for the electrochemical splitting of water [1,2].

TiO_2 was found to be capable of splitting water molecules into oxygen and hydrogen gases in 1972 by Fujishima and Honda [3]. However, owing to its relatively large band gap (3.0 and 3.2 eV for rutile and anatase, respectively), photovoltaic application of this photocatalyst is limited to the ultra-violet portion of the electromagnetic spectrum. The quantum conversion efficiency of TiO_2 can be enhanced if its band gap is made to absorb in the visible range. To achieve this there have been several efforts to dope the oxide and therefore introduce new energy levels into the band gap [4] allowing it to absorb light in the visible region. The substitutional doping of TiO_2 with transition metals [4] and with anion impurities [5] have often enhanced its photocatalytic performance. However, transition metal dopants often create localized deep d states in the TiO_2 band gap that are generally responsible for reducing charge-carrier lifetime due to an increased recombination rate thereby decreasing efficiency.

Among all dopants tested, nitrogen is consistently recognized as one of the most effective dopants, both theoretically and experimentally. The electronic structure study of N doped TiO_2 by Asahi [5] based on the density of states (DOS) calculations reveal that substitutionally doping TiO_2 with N creates localized N_{2p} states just above the valance-band edge. This results in a mild reduction in the band gap (~ 0.2 eV) and red shifts the optical absorption edge by about 100 nm beyond the UV region. The key element in understanding these materials is in fully understanding their electronic structure.

Figure 1 shows the band gap calculated from diffused reflectance measurements as a function of N doping in TiO_2 synthesized by reactive pulsed laser deposition [6]. Other works have shown evidence for band gap

reductions from samples synthesized by different techniques [7, 8]. However, the reasons for the observed band-gap change still remain debated. Asahi et al [5] proposed a narrowing of the TiO_2 band gap due to the hybridization of O and N $2p$ states in the valence band. This can be attributed to the natural extension of the valence-band maximum to lower binding energy, since the N $2p$ level has lower binding energy relative to O $2p$. More recent studies, however, have proposed that the dopant N $2p$ orbital forms a localized state just above the valence-band maximum of O $2p$.

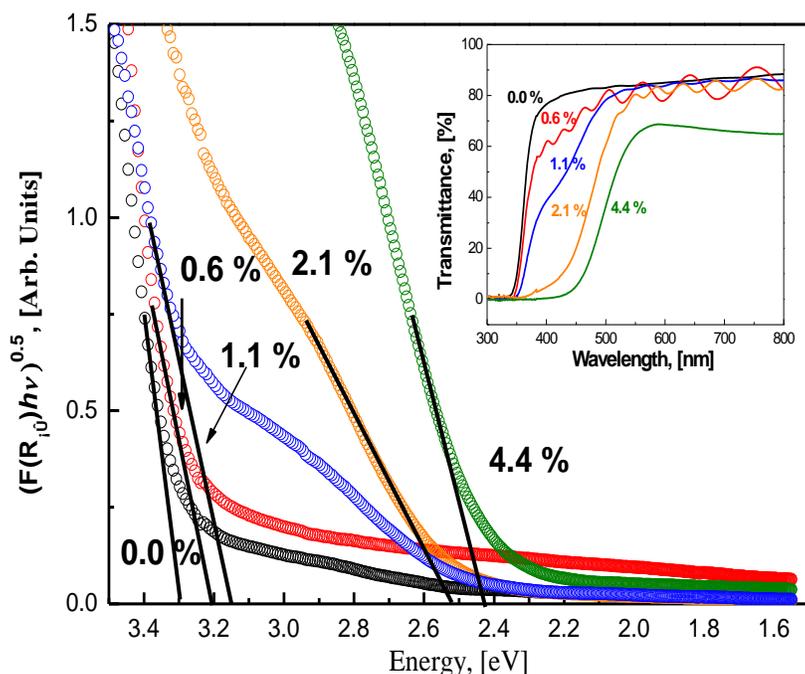


Figure 1: Band gap approximation using transformed Kubelka Monk function. Insert is the corresponding optical transmittance spectra for all samples.

HAXPES measurement performed on NIST beamline X24A at the NSLS gave unambiguous determination of the electronic structure of N doped TiO₂ [9]. Comparing bulk sensitive, valence-band HAXPES measurements (recorded with photon energy $h\nu = 2140$ eV) with ab-initio calculations revealed the

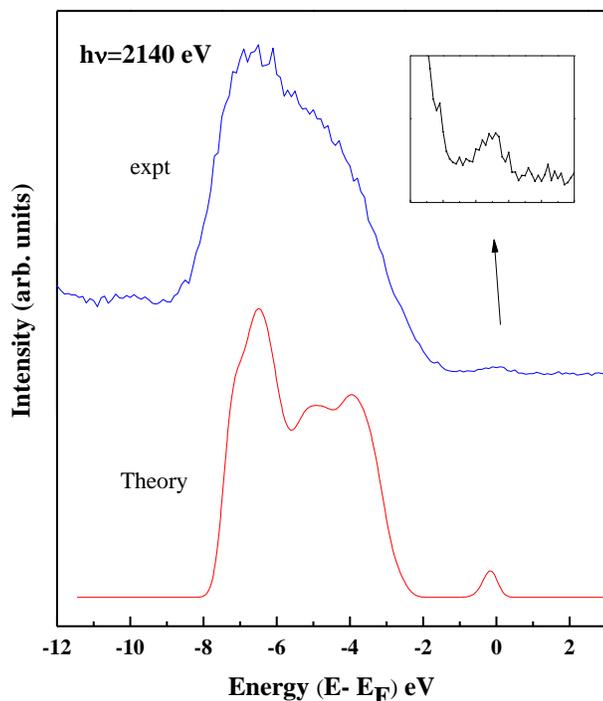


Figure 2: Valence band of N doped TiO₂

role of oxygen vacancies in the doped oxide structure (Figure 2). It was shown that near a N substituted atom it was energetically favorable for an oxygen vacancy to form. The excess electrons, due to the oxygen vacancies, occupy the Ti 3d states near the Fermi level, as seen in Figure 2. Although the valence band structure shows tailing to lower energies due to the incorporation of less tightly bound N 2p which is hybridized with O 2p causing a reduction in band gap, the shift is not large enough to account for the measured change in band gap from reflectivity data (Figure 1). It therefore is concluded that the combination of N impurity and O vacancy is responsible for the UV-vis absorption response in the visible region.

This measurement shows the power of HAXPES in studying bulk electronic structure, and, in particular, the changes in electronic structure upon bulk doping owing to the reduced surface sensitivity of higher kinetic energy photoelectrons in a HAXPES experiment. Conventional, low photon-energy, surface-sensitive measurements employ Ar⁺ etch to clean the surface. This method leads to preferential etching of oxygen and the natural formation of oxygen vacancies. Thus it becomes impossible to resolve the origin of the vacancies in a low energy photoemission experiment.

Our work has showed that oxygen vacancy creation is due to N doping (charge compensation) and is present within the bulk of the sample.

Significant future studies of the change in the electronic structure of transition-metal oxides with dopant incorporation and the advance of theoretical simulations of electronic structure should follow from the development of the NIST soft and tender beamline for hard x-ray photoelectron spectroscopy (HAXPES). This beamline will offer higher photon energies (up to 7.5 keV) with better experimental resolution than currently available at X24A. In particular, as demonstrated, HAXPES allows the study of bulk electronic structure from samples introduced from air without surface treatment which may perturb both their atomic and electronic structures.

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**Correlating the Geometric and Electronic Structure of Nanomaterials:
Finite Size Effects for Tailoring Materials Properties**
Sarbjit Banerjee (Department of Chemistry, SUNY Buffalo)

I. Graphene: Probing Electronic Structure to Inform Device Design

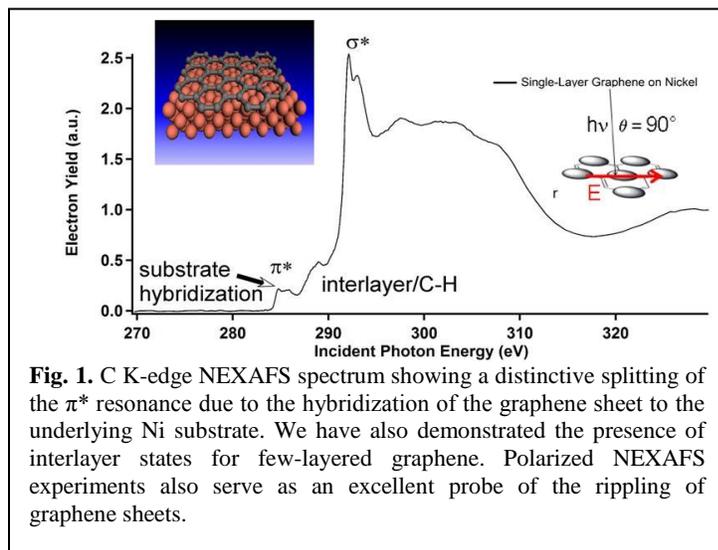
Graphene, a one-atom thick, two-dimensional (2D) electronic material constituted from a single layer of carbon atoms tightly packed within a honeycomb lattice, has few parallels in condensed matter physics. It has captured the attention of scientists and engineers because of its unique electronic structure and the resulting possibilities for novel device concepts and technological paradigms originating from its massive carrier mobilities, size-tunable band gaps, and room-temperature quantum transport phenomena (Geim, A. K. and Novoselov, K. S., *Nat. Mater.* 6 (3), 183-191, 2007).

As major breakthroughs are achieved in the scalable fabrication of graphene, fundamental studies of graphene interfaces are entering the realm of possibility. Specifically, being a one-atom thick layer, it is to be expected that interfacial phenomena will strongly impact its electronic structure and carrier transport. ***The proposed NIST NSLS-II combined XPS/NEXAFS and imaging capabilities would meet an urgent need to develop localized and global probes that can be used to simultaneously probe valence- and conduction-band structures as well as the Fermi level with high spatial resolution as a function of different perturbations applied at graphene interfaces.***

The University at Buffalo, SUNY team has been investigating the conduction band structure of graphene in collaboration with the NIST Synchrotron Methods Group and the Front-End Process Division at SEMATECH. Our preliminary polarized ***NEXAFS spectroscopy and imaging*** studies of graphene prepared by chemical vapor deposition and solution exfoliation routes have yielded a wealth of information regarding the substrate hybridization, surface chemistry, and local corrugation of graphene.

Our findings include: **(a)** Evidence for strong hybridization of graphene π^* states to the d_{z^2} orbitals of underlying Ni and Cu substrates (Fig. 1) (Lee, V., et al., *J. Phys. Chem. Lett.* 1, 1247-1253, 2010.); **(b)** graphene grown on Cu shows a high degree of substrate alignment but significant rippling is introduced during transfer to SiO_2/Si substrates; **(c)** the π^* structure of chemically derived graphene is substantially restored upon the reduction of exfoliated graphene oxide (Lee, V., et al., *Chem. Mater.* 29, 3905-3916, 2009); and **(d)** a comparative NEXAFS evaluation of the efficacy of different reducing agents in defunctionalization and restoration of the conjugated graphene π^* network has been performed and has informed the development of solution-chemistry routes for the preparation of large-area graphene (currently being commercialized for indium tin oxide (ITO) replacement and for graphene-based acrylics for aircraft windows by UB in collaboration with Graphene Devices Limited). The chemically derived graphene technologies based on solution processes for exfoliating and defunctionalizing graphene oxide are of tremendous importance for the large-scale fabrication of graphene for use in nanocomposites with potential applications in armor or electromagnetic interference shielding. In addition, fundamental studies of high-quality graphene prepared by CVD are instructive in identifying electronic interactions at key graphene interfaces such as will be found in the next generation of electrical interconnects and high electron mobility transistors.

Currently, there is a significant gap in our understanding of how the valence and conduction band states of graphene are modified by perturbations such as the *formation of metal, dielectric, semiconductor, and molecular interfaces. Being simultaneously able to perform XPS and NEXAFS measurements* of the same



sample region will enable the development of a comprehensive picture of how the valence and conduction band structures are altered such as upon deposition of an overcoating thin dielectric layer or by hybridization to an underlying substrate. For example, an angle-resolved comprehensive XPS and NEXAFS study of graphene grown on different transition metals will be performed and in conjunction with density functional theory (DFT) modeling of graphene/metal interfaces will help in the derivation of a map of the relative strength and directionality of graphene/metal bonding.

The potential to modify the electronic structure of graphene via the pi-stacking of extended aromatic molecules represents a particularly tantalizing possibility that will also be explored by the same combination of XPS, NEXAFS, and DFT modeling. XPS chemical shifts of the adsorbed molecules in conjunction with NEXAFS evidence for hybridization to graphene will enable the development of chemical routes to modulating the electronic structure of graphene with significant potential impact in organic electronics.

The increased corrugation and rippling of graphene—related to coupling with the underlying substrate or membrane bending introduced during a transfer process—deleteriously impacts the mobilities of charge carriers. It has been predicted that electrons propagating through graphene are scattered by corrugations and ripples in the graphene sheet through a potential approximately proportional to the square of the local curvature. Polarized NEXAFS measurements are incredibly sensitive to the rippling of graphene. *The proposed unprecedented spatial resolution of NIST's NEXAFS imaging will allow the acquisition of high spectral resolution NEXAFS data accurately pinpointing the location of graphene asperities (Patridge, et al., in preparation, 2010).*

For chemically derived graphene, the NEXAFS imaging capabilities will allow unprecedented chemical mapping of the location of functional groups. Combined XPS and NEXAFS studies will enable the conclusive identification of graphene functional groups retained after defunctionalization with various reducing agents, thus resolving a longstanding controversy over the nature and relative concentrations of different graphene surface functional groups and their NEXAFS spectral signatures.

II. Nanostructured Vanadium Oxides: Correlating Geometric and Electronic Structure to Massive Electronic Instabilities

Metal—insulator transitions in strongly correlated materials, induced by varying either temperature or dopant concentration, remain a topic of enduring interest in solid-state chemistry and condensed matter physics owing to their fundamental importance in answering longstanding questions regarding correlation effects and the possible generalizability of the underlying mechanisms to explain a wide range of quantum transport and spin phenomena including superconductivity (Qazilbash, M. M., et al., *Science* 318, 1750-1753, 2007; Imada, M., et al., *Rev. Mod. Phys.* 70, 1039-1263, 1998). Furthermore, the underlying operating principles for a diverse array of technological applications ranging from switching elements and thermochromic coatings to Mott field-effect transistors and infrared modulators essentially involve the thermal or voltage-driven induction of an insulator—metal transition.

In this context, the University at Buffalo, SUNY team has been collaborating with the NIST Synchrotron Methods group to explore correlation effects and electronic instabilities that arise from scaling vanadium oxides to the nanometer-size regime. Vanadium oxides have a rich and complex phase diagram originating from the facile accessibility of different vanadium oxidation states and the various structural distortions adopted to accommodate non-stoichiometry and point defects (Chernova, N. A., et al., *J. Mater. Chem.* 19 (2526-2552), 2009).

Understanding the influence of finite size on the phase stabilities will not only contribute to fundamental understanding of the remarkable phase transition behavior, but significantly, our preliminary results (Fig. 2) indicate that scaling materials to nanoscale dimensions also offers the tantalizing possibility of enabling the observation of novel single-domain phenomena that are otherwise obscured in bulk samples.

In the absence of single-crystal diffraction data or detailed atomistic simulations, very little is known about subtle changes in the electronic ($V-O$ rehybridization, extent of charge disproportionation) and geometric structure (lattice expansion/contraction, defect density, surface reconstruction) of vanadium oxides induced as a result of scaling to the nanometer-sized regime. Subtle changes in geometric and electronic structure are likely implicated in the strong modifications to the metal-insulator phase transition temperatures and hysteresis widths observed for the archetypical phase transition material VO_2 as well as novel $M_xV_2O_5$ nanostructures upon scaling to finite size and substitutional/intercalative doping. **The proposed NIST NSLS-II beamlines will significantly**

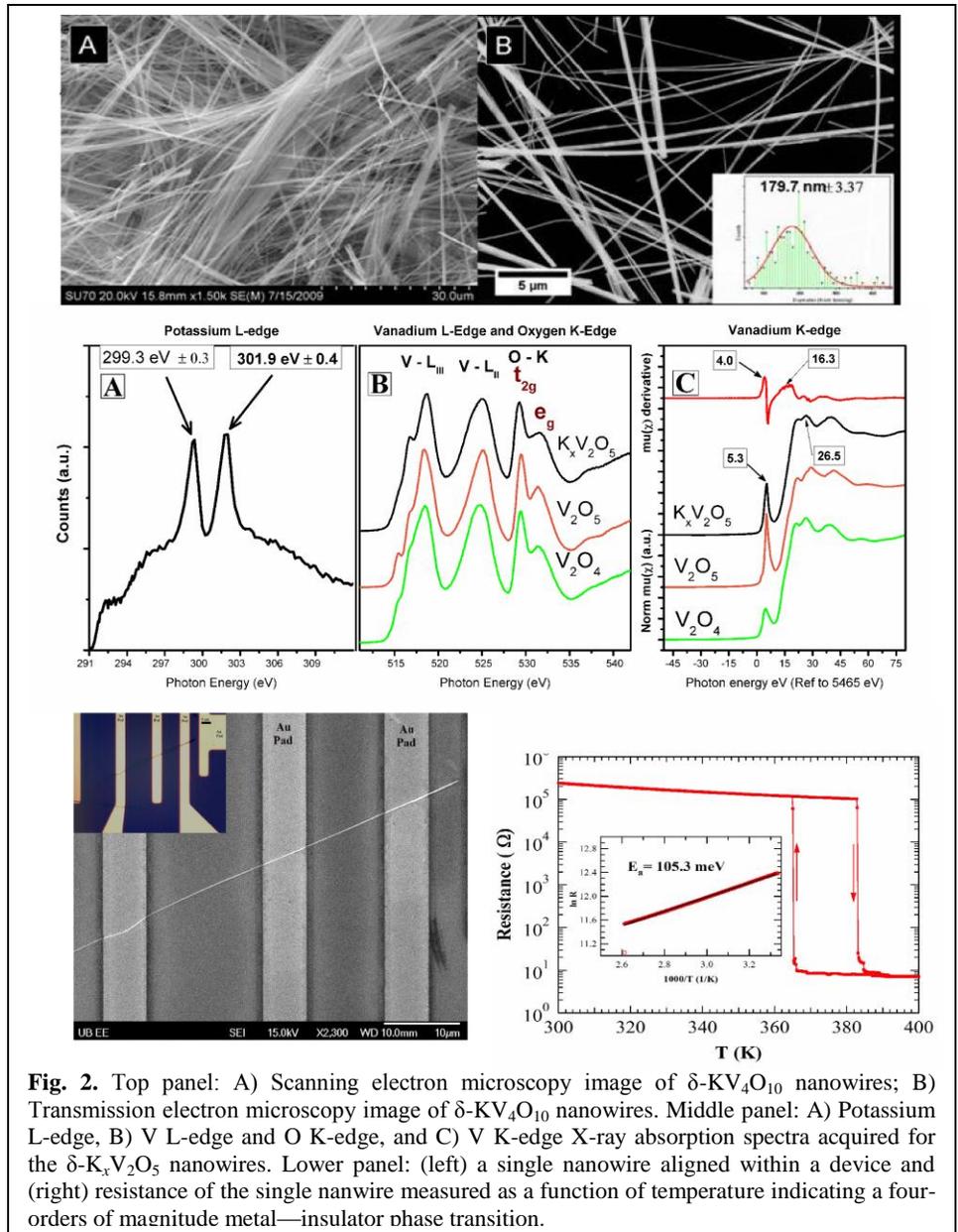


Fig. 2. Top panel: A) Scanning electron microscopy image of δ - KV_4O_{10} nanowires; B) Transmission electron microscopy image of δ - KV_4O_{10} nanowires. Middle panel: A) Potassium L-edge, B) V L-edge and O K-edge, and C) V K-edge X-ray absorption spectra acquired for the δ - $K_xV_2O_5$ nanowires. Lower panel: (left) a single nanowire aligned within a device and (right) resistance of the single nanowire measured as a function of temperature indicating a four-orders of magnitude metal-insulator phase transition.

impact the fields of solid-state chemistry and condensed matter physics of nanoscale correlated materials by enabling simultaneous measurements of geometric and electronic structure using V L_{III} , L_{II} and O K-edge NEXAFS measurements using soft X-rays and V K-edge measurements using tender X-rays for the same sample across the metal-insulator transition temperature. The XANES features will provide valuable insight into solid-state dispersion effects and enable the mapping of the delocalized conduction band states derived from p orbitals, whereas the EXAFS features will allow development of detailed atomistic understanding of the vanadium coordination environment. Additionally, XPS measurements as a function of temperature will allow the formal valence distribution of different vanadium sites to be measured across the metal-insulator phase transition.

Notably, we have developed a solvothermal synthetic protocol for the facile and high-yield synthesis of doped and undoped VO_2 and various $M_xV_2O_5$ phases where $M = Na, K, Cu,$ and Zn . The VO_2 nanostructures show a pronounced depression and large hysteresis for the metal-insulator phase transition upon scaling to nanometer-sized dimensions or doping with tungsten. As for the non-stoichiometric $M_xV_2O_5$ bronzes, we have observed a hitherto undiscovered four orders of magnitude near-room-temperature metal-insulator phase

transition in nanostructures of a novel δ -KV₄O₁₀ phase with remarkable stochastic switching between the phases near the phase transition temperature (Patridge, C. J. et al., *Nano Lett.*, in press, 2009). This material thus represents a rare new addition to the pantheon of materials exhibiting pronounced metal—insulator transitions in proximity to room-temperature.

Some of our published findings on the electronic structure of vanadium oxides indicate (a) the d_{xy} origin of the conduction band of V₂O₅ deduced using angle-resolved NEXAFS measurements of highly oriented V₂O₅ nanowires (Velazquez, J. M. et al. *J. Phys. Chem. C* 113, 7639-7645, 2009.); (b) massive hysteresis in electronic structure concurrent with changes in geometric structure for VO₂ nanowires (Whittaker, L., et al. *J. Am. Chem. Soc.* 131, 8884–8894, 2009), and (c) evidence for room-temperature charge disproportionation and reduction of specific vanadium sites from V⁵⁺ to V⁴⁺ upon the intercalation of alkali or transition metal ions in Cu_xV₂O₅ and δ -KV₄O₁₀ bronze nanostructures (Patridge, C. J. et al., *Nano Lett.*, in press, 2009; Patridge, C. J., et al. *Inorg. Chem.* (48), 3145-3152, 2009). Figure 2 shows some potassium L-edge, vanadium L-edge, oxygen K-edge, and vanadium K-edge data acquired at the NIST beamlines U7A and X23A2 of the NSLS for δ -KV₄O₁₀ nanowires along with electrical transport data showing pronounced metal—insulator phase transitions.

The proposed soft/tender NIST beamlines at NSLS-II will have a pronounced impact on our understanding of changes in electronic and geometric structure that accompany scaling to finite size and will help explain the strong alterations to metal—insulator phase transition temperatures and hystereses observed for vanadium oxide nanostructures. Specifically

- (i) **The combination of soft- and tender-X-ray beamlines will allow** simultaneous acquisition of both XANES and EXAFS data at the V L-edge, O K-edge, and V K-edge and possibly also at K- or L-edges of dopant or intercalant atoms. This will enable both the geometric and electronic structure of VO₂ and M_xV₂O₅ nanostructures to be simultaneously studied.
- (ii) Combined XPS and NEXAFS measurements across the phase transition will allow the development of a comprehensive picture of the electronic structure.
- (iii) **The high-throughput microscopes will allow simultaneous acquisition of XANES, EXAFS and XPS data** at various edges such as shown in Fig. 2 in a single experiment and will thus enable structure—function correlations to be developed for nanowires with varying stoichiometry, dimensions, and morphology.

For example, it will be possible to explore the electronic structure of nanostructured vanadium oxides across the metal—insulator transition using 1s → 2p transitions (probing relatively more delocalized states) via NEXAFS spectroscopy at the O K-edge and XANES measurements at the V K-edge. Furthermore, NEXAFS data acquired at V L_{III,II}-edges corresponding to transitions from 2p→3d states will be valuable in understanding the conduction band features involved in transport and optoelectronic material properties.

Perhaps even more informative than the XANES features will be the oscillations observed >40 eV above the absorption edge, the EXAFS. EXAFS oscillations will be best-fitted to obtain values of nearest neighbor and next-nearest neighbor distances (out to about 5 Å from the excited atom), the coordination number, and the disorder in the distances for each coordination shell. Clearly, this will yield a wealth of local structural information and enable subtle changes in lattice parameters to be detected. Further, XPS measurements as a function of temperature will allow the formal valences of different vanadium sites to be mapped across the metal—insulator phase transitions for VO₂ and M_xV₂O₅ and will shed light into the critical V⁴⁺/V⁵⁺ ratio required to trigger instabilities at the Fermi level that give rise to pronounced metal—insulator phase transitions.

Detailed structure—function correlations established in these experiments will pave the way for the design of vanadium oxide nanostructures with optimal dimensions, morphology, and composition that exhibit tunable metal—insulator phase transitions at specific temperatures with well-defined magnitudes.

NEXAFS Imaging of Propagating Waves of Self-Assembly in Organosilane Monolayers

Jan Genzer, NC State University

Impetus. Wave-fronts associated with reaction-diffusion and self-assembly processes are ubiquitous in the natural world. For instance, propagating fronts arise in crystallization and diverse other thermodynamic ordering processes. In biology, propagating fronts influence cell movement and division, as well as in the competitive social interactions and population dynamics of animals at much larger scales see Figure 1 below. While it is often claimed that self-sustaining or *autocatalytic* front propagation is well-described by mean-field ‘reaction-diffusion’ or ‘phase field’ ordering models, recent simulations and theoretical arguments show that *fluctuation effects* in lower spatial dimensions can lead to appreciable deviations from the classical mean-field theory of this type of front propagation. While these observations have significant implications for diverse types of ordering fronts that occur under confinement conditions in biological or materials-processing contexts, not much is known about the molecular aspects of this process. In collaboration with NIST, our groups has recently carried out preliminary experiments aimed at providing some missing links to the picture using a model system based on directional self-assembly of organosilane (OS) molecules on surfaces. Specifically, we reported that these OS adlayers organize from the substrate edge as *propagating wave-fronts* having well-defined velocities and shapes.⁴¹ While these initial experiments offered valuable insights that may be applicable to any autocatalytic front propagation process, much more work needs to be done in order to gain detailed understanding of the assembly and dynamics of OS precursors deposited from vapor phase in a directional manner onto flat solid silica substrates.

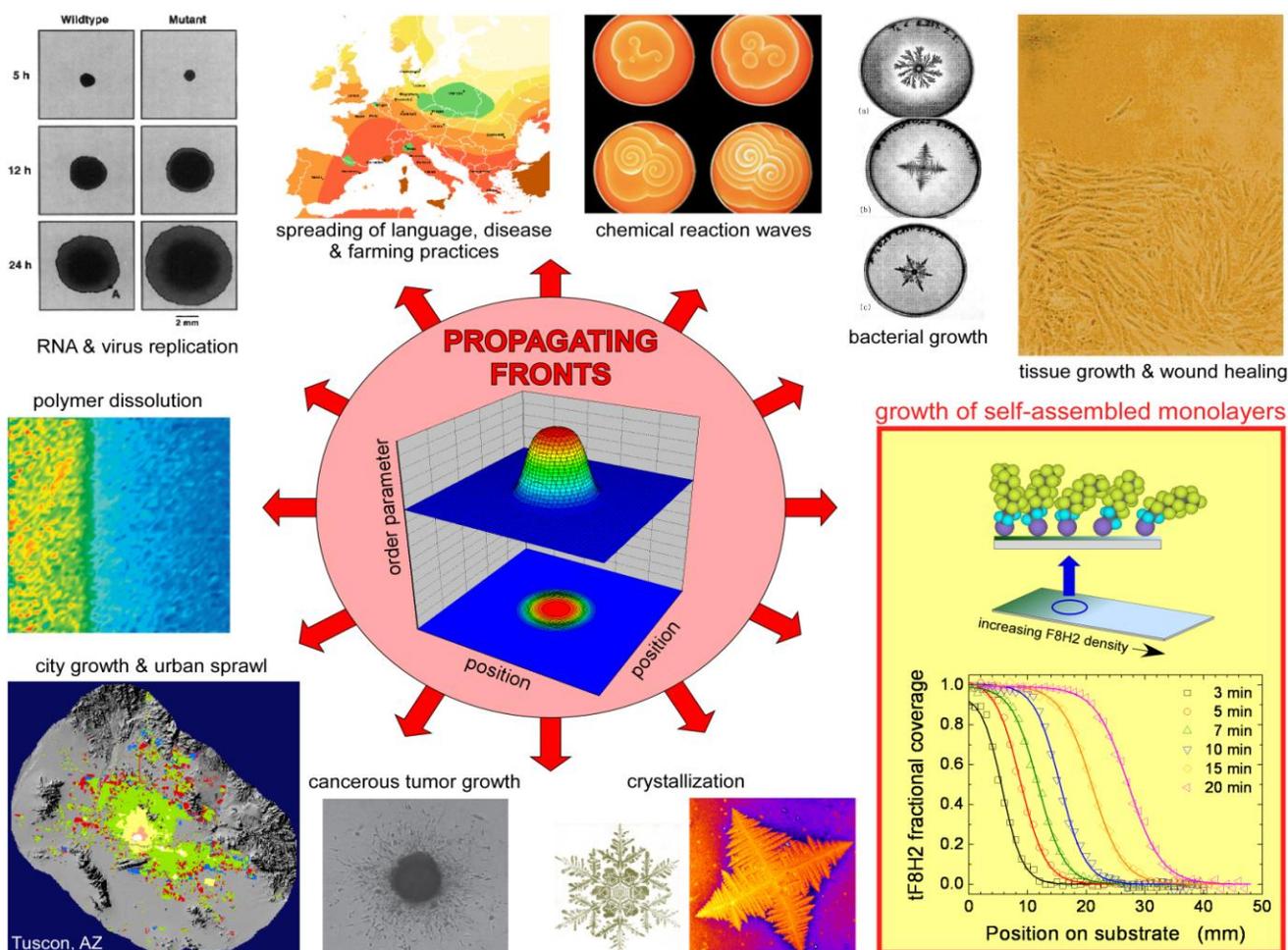


Figure 1. Examples of propagating fronts. See http://www.engr.ncsu.edu/news/news_articles/waveprop.html

⁴¹ J.F. Douglas, K. Efimenko, D.A. Fischer, F.R. Phelan, J. Genzer, Propagating waves of self-assembly in organosilane monolayers”, *PNAS*, **104**, 10324 (2007).

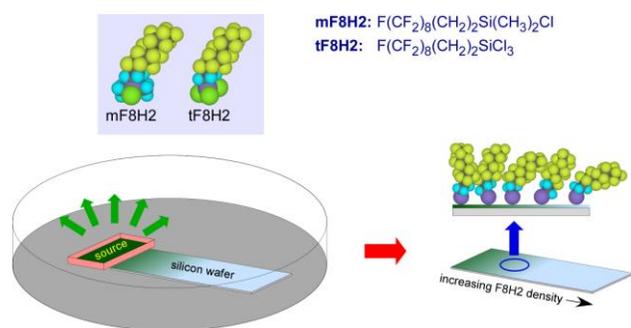


Figure 2. Schematic illustration of surface energy gradient formation in SAM layers. The average angular orientation of the molecules directly tracks the OS concentration and thus the normalized local concentration is identified with an order parameter for SAM ordering.

gradient of the OS molecules on the substrate that provides a direction to the self-assembly process. The geometry of the container modulates the nature of this gradient and the type of organization that occurs.⁴⁵ With increasing time, further OS molecules are deposited on the surface and the position of the maximum in the gradient in the molecular concentration and SAM ordering (*i.e.*, the interface between the assembled and non-assembled regions on the substrate) progresses across the substrate. Upon landing and molecular reorganization, the OS molecules react with the surface-bound -OH groups; the gradient is fixed into position by removing the OS source. We have recently argued that this kind of molecular self-assembly provides an example of a generic autocatalytic organizational process.⁴¹ We provided indirect but sound experimental evidence from scaling experimentally-measured diffusion profiles and comparing them to predictions of computer simulations modeling autocatalytic fronts in confined spaces. Importantly, our work suggested that when the aforementioned deposition process is carried out under confinement (Petri dish container) it exhibits autocatalytic nature. We contrasted this behavior to the case where the deposition under “no confinement” (inverted 2-liter beaker) produced concentration profiles of surface-bound OS that can be very reasonably described using a classical Fickian diffusion model.

We plan to study the effect confinement on wave-front development due to in-plane constraints present on the substrate. The diffusing fronts will be formed using semifluorinated OS molecules both in the confined and unconfined geometries. The concentration of the deposited OS molecules in the wave-fronts will be monitored with *NIST's Large Area Imaging NEXAFS Microscope*, a new experimental technique recently developed at the NIST's NSLS Beamline U7A. The *NEXAFS Microscope* represents a much improved combi-NEXAFS,⁴⁶ it takes snapshots of Auger electrons as a function of the photon energy across substrates of $\approx 12 \times 18 \text{ mm}^2$. The collection time is fast, it takes about 8 minutes to collect NEXAFS image spectra with sufficiently high counts. This is important in order to minimize any damage to the samples due to x-rays (semifluorinated OS are particularly sensitive to these effects.⁴⁷). By combining images from neighboring areas at various angles θ , the

Approach. We utilize a method of creating self-assembled monolayers (SAMs) using OS molecular gradients^{42,43}, proposed by Chaudhury and Whitesides (*cf.* **Figure 2**).⁴⁴ Rather than employing a solution as a carrier for the depositing SAM molecules, Chaudhury and Whitesides simply placed a drop of high vapor pressure OS at the edge of a silica-covered substrate and enclosed the entire system in a Petri dish container to avoid convection effects. As the OS molecules traverse through the atmosphere above the substrate, the molecules ‘rain down’ and self-assembled spontaneously on the substrate. The *symmetry breaking* associated with placing the source of diffusing material to the side of the wafer leads to the initial formation of a concentration

⁴² J. Genzer, “Molecular gradients: Formation and applications in soft condensed matter science,” in *Encyclopedia of Materials Science*, (K.H.J. Buschow, R.W. Cahn, M.C. Flemings, B. Ilshner, E.J. Kramer, S. Mahajan, eds., (Elsevier, Oxford, 2002).

⁴³ J. Genzer, R.R. Bhat, T. Wu, K. Efimenko, “Molecular gradient nanoassemblies,” *Encyclopedia of Nanoscience & Nanotechnology*, (H. S. Nalwa, ed.), American Scientific Publishers, Vol. 5, pp. 663-676 (2003).

⁴⁴ M.K. Chaudhury, G.M. Whitesides, “How to make water run uphill,” *Science* **256**, 1539 (1992).

⁴⁵ J. Genzer, K. Efimenko, D.A. Fischer, “Formation mechanisms and properties of semifluorinated molecular gradients on silica surfaces,” *Langmuir* **22**, 8532 (2006).

⁴⁶ J. Genzer, D. A. Fischer and K. Efimenko, “Combinatorial near-edge x-ray absorption fine structure: Simultaneous determination of molecular orientation and bond concentration on chemically heterogeneous surfaces”, *Applied Physics Letters* **82**, 266 (2003).

⁴⁷ B. Jäger, et al., “X-ray and low energy electron induced damage in alkanethiolate monolayers on Au-substrates”, *Phys. Chem.* **202**, 263 (1997); M. Wirde, et al., “Modification of self-assembled monolayers of alkanethiols on gold by ionizing radiation”,

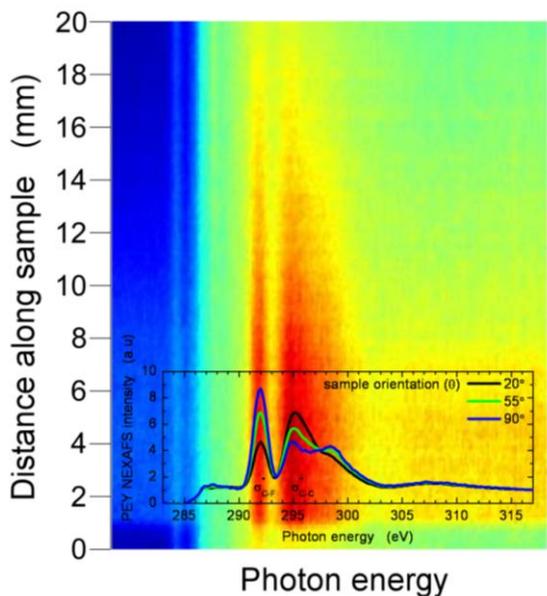


Figure 3. Electron yield intensity in imaging NEXAFS collected along tF8H2 gradient (distance 2 cm) at $\theta=50^\circ$. The red stripes correspond to the $1s \rightarrow \sigma^*_{C-F}$ and $1s \rightarrow \sigma^*_{C-C}$ transitions in tF8H2; their decreasing intensity across the sample is due to the presence of the decreasing concentration of tF8H2. For clarity, we superimpose typically NEXAFS spectra collected from homogeneous tF8H2 SAMs collected at three different angles θ .

compositional and orientation map can be obtained from the entire specimen. In **Figure 3** we plot an example of a compositional map collected from a tF8H2 gradient as a function of the position on the sample (ordinate). Note the position-dependent decrease in the intensity at 292 and 296 eV, corresponding to the $1s \rightarrow \sigma^*_{C-F}$ and $1s \rightarrow \sigma^*_{C-C}$ transitions. The current lateral resolution of the technique is $\approx 80 \mu\text{m}$; this is sufficiently good for measuring the concentration of OS molecules in narrow wells on the substrate. The newly proposed **NEXAFS Microscope** instrument for NIST' that will be part of NIST's SST beams at NSLS II will promise further enhancement of the capabilities of this unique instrument. With a scanning area of $20 \times 20 \text{ mm}^2$ and lateral resolution at $1 \mu\text{m}$, we may even be able to visualize the concentration fluctuations at the wave-front directly with this exceptional analytical probe. There is no doubt that new important information about self-assembly processes (including, lateral distribution, chemical composition and molecular orientation) will be gathered that will enable much needed information about ubiquitous molecular assembly on surfaces.

Potential impact. Many molecular processes as well as the population dynamics of humans and other organisms can be described in terms of fundamental 'entities' undergoing random local displacement events. These exhibit regular motion at large

scales and associated pattern formation as the participating entities collectively move from some unstable situation to a relatively stable state of greater energetic or competitive 'advantage'. These pattern formation processes are ubiquitous in the natural world and largely govern successive waves of evolutionary development. **Figure 1** depicts a few such examples. Since the spreading of autocatalytic waves is a pervasive phenomenon, modeling and analogies conceived to describe them can be applied to other everyday 'invasive' phenomena, *e.g.*, the introduction of foreign plant species into new environments, triggering waves of invasive growth in the countryside, the growth of urban sprawl, frontal polymerization, corrosion of metallic films, polymer dissolution, and many others (*cf.* **Figure 1**). Fluctuation effects tend to make these fronts increasingly incoherent (diffuse) in time, and thus are expected to greatly impact the *interactions between* frontal patterns under conditions where species (or different types of ordering) are competing for supremacy. Indeed, the *interaction* of two counter-propagating autocatalytic wave-fronts is one of the key areas we plan to study in this work. To that end, **NEXAFS Microscope** at the NSLS II will be a key instrument we plan to utilize in our work.

The NIST Full Field XPS Magnetic Projection Microscope (XPS-MPM): Chemical and structural imaging at 1nm using a new class of microscope

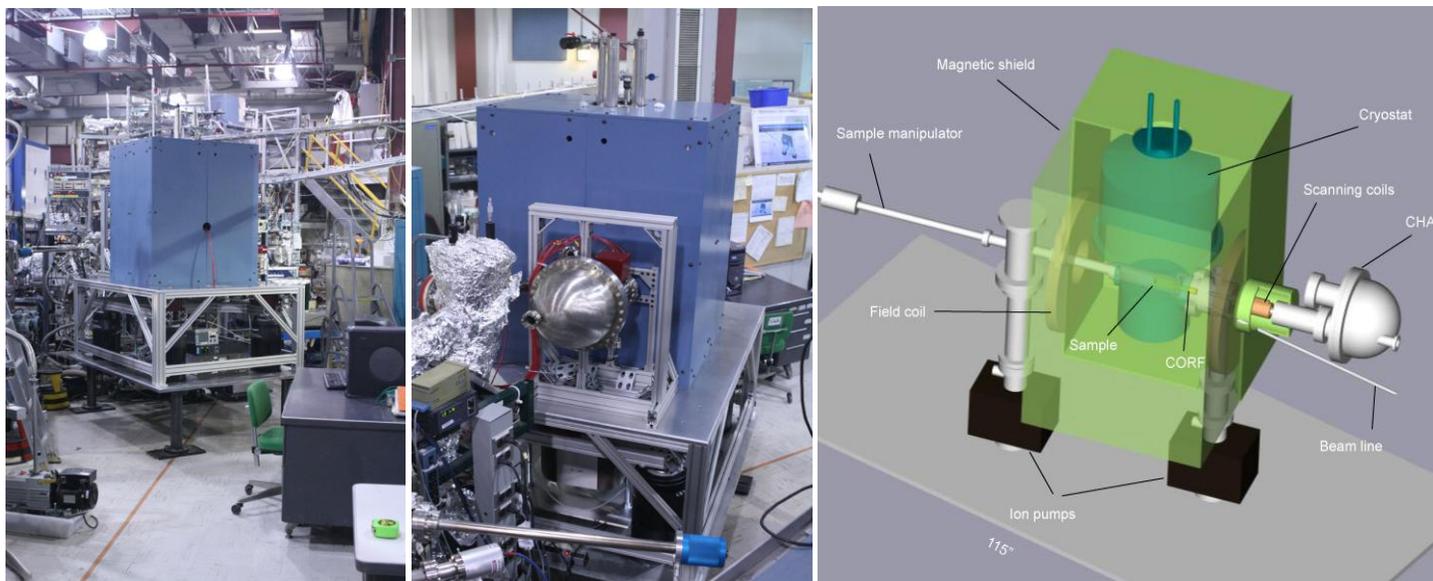
Raymond Browning (R. Browning Consultants) and Daniel Fischer (NIST)

Our objective is to create a new chemical measurement microscope and NIST user facility at NSLS II to advance the development of functional nano-materials such as organic photo-voltaics, and novel catalytic systems for energy conversion and storage, and nanoelectronics (CMOS and beyond). The target spatial resolution will be **1nm** for nondestructive, **in-situ**, 3 dimensional (**3D**) chemical and structural imaging.

Our approach is to continue development of the new class of X-ray photoelectron microscope that R. Browning Consultants has invented under NIST SBIR contracts (currently 3 US patents awarded, and four applications). This new class of photoelectron microscope (US Pat. 7,718,961) has several major developments in electron optical design that distinguish it from previous microscopes, including: a cyclotron orbit radius filter (US Pat. 7,608,838), a magnetic field terminating electron spectrometer (US Pat. 7,569,861), and an integrated magnetic shield and projection lens (Patent applied for). These, and other developments, will lead to a first in class facility.

The development of the new microscope, a full field imaging X-ray Photoelectron Spectroscopy Magnetic Projection Microscope (XPS-MPM), will be in stages leading to a 1nm imaging tool and General User Facility at the state-of-art NIST beamlines at NSLS-II.

NSLS-II high brightness undulator beamlines will be critical for this microscope, opening the door for a wide range of applications. A key beamline element is sufficient brightness over a wide tunable range of energies. The imaging technology can be developed such that chemical, electronic, and structurally specific signals can be simultaneously extracted from the multiple photoemission core levels. The proposed NIST NSLS-II Soft and Tender beamlines with its continuous selection of X-rays from 100 eV to 7.5 keV gives access to these core levels, and with sufficient flux to provide 1nm resolution, with nondestructive 3D chemical imaging by varying the kinetic energy of the photoelectron. The unique XPS-MPM optics also has a wide field of view, a large depth of focus, and thus will be suitable for many real world industrial samples including ambient pressure catalysis studies. The NIST XPS-MPM at NSLS-II is expected to enable advances in virtually all materials (polymeric, inorganic, and biologic) and devices for myriad applications.



Full field NIST XPS magnetic projection microscope under development by R. Browning Consultants funded under NIST Small Business Innovation Research grants at NSLS beamline U4A

US Patents: Inventor: R. Browning

7,569,861 'Electron Spectrometer' August 4, 2009

7,608,838 'Electron Optical Component' October 27, 2009

7,718,961 'Photoelectron Microscope' May 18, 2010

The XPS-MPM can be compared to photoelectron emission microscopy (PEEM) to illustrate the power of the technique. The table below gives an overview of the major advantages given by the magnetic projection lens of the XPS-MPM over the high voltage electrostatic immersion lens of PEEM. These advantages, can be summarized by the XPS-MPM having applications over a wide range of sample types of direct relevance to industry.

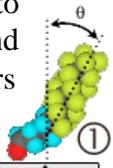
	PEEM 2D chemical and magnetic imaging on flat conducting surfaces Surface Science Method based on high voltage electrostatic immersion lens with the sample as part of the lens, best resolution for very low energy photoelectrons and very flat surfaces	NIST XPS-MPM 3D+ chemical, chemical phase, and structural imaging on many surfaces, General Industrial User Method based on magnetic projection lens, resolution relatively independent of sample type, and photoelectron energy
Ultimate Resolution	3-5nm. Good theoretical and test piece resolution - down to 3nm on latest instruments. 50nm more common in practice	1-5nm. UPS and XPS ultimate resolutions below 10nm expected on most samples
Depth of Field	Small. Small depth of field. Flat surfaces if chemical contrast is required. Topography is a strong contrast mechanism that degrades resolution	Very Large. Large depth of field. 1-2mm, Topographic contrast due to shadowing and projection angle effects, does not degrade resolution
Sample Types	Conducting. Conducting surfaces are required for high resolution, the sample is part of the extraction optics	Multiple surface types, rough non-conducting
Imaging types	Elemental, Chemical, Magnetic	Elemental, Chemical, Phase Analysis, Structural
Field of View	1-100μ	1μ – 2mm
Depth of signal	2 dimensions <1nm very surface sensitive	3 dimensions, 1-10nm tunable with photon energy and surface angle. Non-destructive depth profiling
Time resolved	2ps with streak camera	20ps from beam line NSLS II
Availability	Commercial suppliers	An UNIQUE microscope Commercial XPS microscopes are 5-50μ resolution and lack quantitative image analysis capabilities
Applications	Many well understood applications: Very nice work on magnetic materials, time resolved domain movements	Many novel applications: Post CMOS nanoelectronics, organic photo-voltaics, organic semiconductors, 3D functional material structures, in-situ processing of catalysts
Ambient pressure	No. Not feasible because of high voltage breakdown	Yes. New method with no differential pumping

Four-Dimensional Hyperspectral Chemical Imaging Based Upon Large Area Near-Edge X-Ray Absorption Fine Structure (NEXAFS) Contrast Using State-of-Art Synchrotron Sources at NSLSII

E. Principe and P. Sobol (Synchrotron Research, Inc.) & D. Fischer (NIST)

The Large Area Rapid Imaging Analytical Tool (LARIAT) NEXAFS end station together with the NSLS II synchrotron source and advanced data mining enables critical pathways in the design of nanochemical systems. The LARIAT (NIST SBIR funding) is one key to unlock understanding of nanochemistry based upon directed self-assembly and novel panoramic patterning methods; the foundation of future advanced materials applied to biology, photonics and electronics.

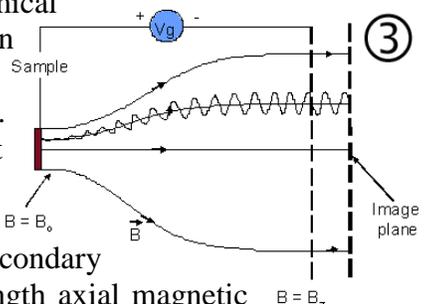
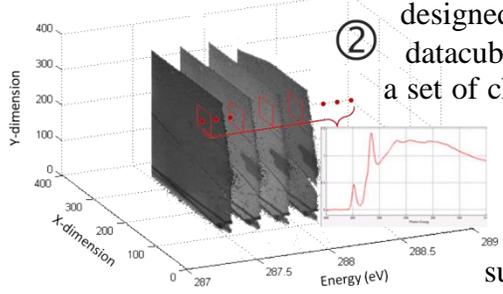
NEXAFS is an established synchrotron-based “near-surface” characterization method uniquely able to provide quantitative information on the nature of chemical bonding (e.g., bond type, bond angle, bond length), molecular concentration and orientation of molecular systems① like self-assembled monolayers (SAMS). Such information is critical to understanding the behavior of new material systems and our ability to control molecular patterns in three dimensions. To that end the NSLS II provides a high brightness tunable energy source (significantly improving data acquisition rates) and an undulator providing polarization control of the electric light vector (expanding the range of information). Reaching the full potential of the new generation NSLS II light source also requires a new generation of analytical end stations compatible with high throughput and efficient data analysis. The LARIAT MKII matches the potential of the NSLS II source with a second generation full field imaging NEXAFS spectrometer



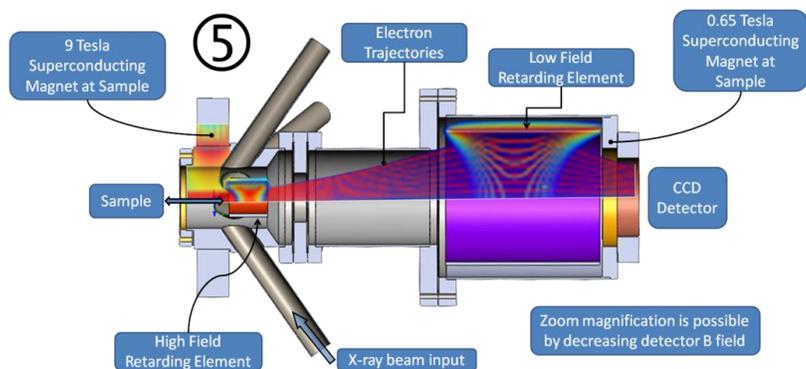
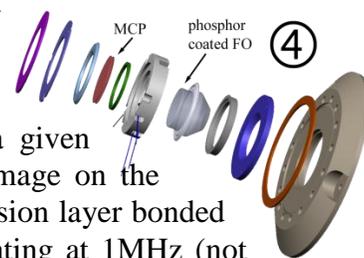
designed for automated parallel acquisition of hyperspectral chemical image datacubes. The term “hyperspectral chemical imaging”② refers to collection of a set of chemical images as a contiguous function of energy, where each image is the result of excitation at a spectrum energy point. Electron energy filtering through the spectrometer discriminates Z-depth information. The X-Y lateral dimensions and Z-depth information combined with the energy spectrum form a four-dimensional datacube. The data may be summed to create high S/N images or spectra can be extracted from any image point as a function of energy.

A large area parallel imaging approach to NEXAFS promotes a new paradigm in design of experiment and combinatorial analysis. While the full field imaging aspect promotes experiments based upon arrays, the spectrometer is also designed for higher throughput to take advantage of the higher brightness of the NSLSII. In about the same amount of acquisition time spent on NSLS I using the LARIAT MKI, the LARIAT MKII on NSLS II will yield a nearly 700X increase in areal information. This improvement is derived from a factor of 1.7 increase in imaging area (400mm²) while simultaneously improving the areal resolution by a factor of up to 400. Collectively these factors further scientific development and enable more efficient use of the synchrotron facilities; science progresses faster at lower cost.

The LARIAT MKII NEXAFS spectrometer produces rapid full field chemical images using a simple elegant design and basic physics principles. Deflection optics scan the synchrotron source beam rapidly across an area up to 20X20mm while the energy is tuned across an absorption edge (e.g., K or L). Resonance at the edge region stimulates a highly sensitive bond dependent yield of electrons across the surface of the specimen, the essence of the NEXAFS process, which the LARIAT detects in parallel. Using an axial magnetic field coupled with a parallel imaging detector the LARIAT detects secondary electrons while preserving their spatial position on the sample. A high strength axial magnetic field (\vec{B}_0) immersing the sample couples to a lower magnetic field at the detector plane (\vec{B}_z). Diverging magnetic flux lines (\vec{B}) couple the fields between the two coils as shown ③. A voltage V_g applied to electrostatic elements form a high pass energy filter for electrons with axial energy, E_a , below V_g . The stimulated electrons emanating from all angles and areas of the sample are forced to follow helical paths around the magnetic flux lines shown in ③. In the schematic the path appears as a sinusoidal curve with increasing amplitude, but it is actually an expanding helix in three dimensions. This helix is formally the electron

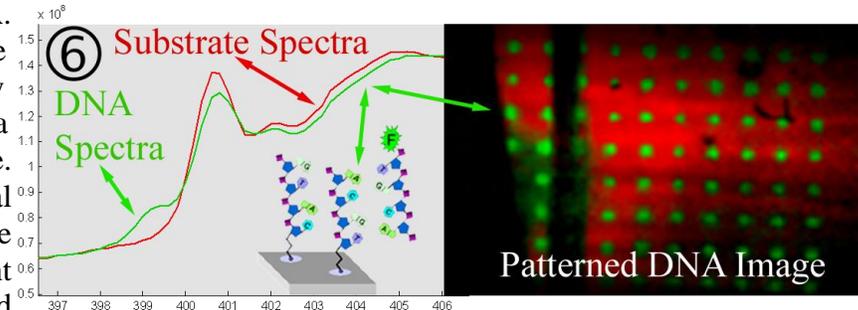


cyclotron radius (ECR) and for an electron with transverse energy E_T ; $ECR_{max} \propto \sqrt{E_T} \div \vec{B}$. It is the ECR at the sample that to first order determines the lateral resolution of the spectrometer. A larger magnetic field at the sample produces a smaller ECR and hence higher lateral resolution at a given electron energy. The coupled fields allow the electrons to form a coherent image on the detector, which is comprised of a micro channel plate (MCP), a phosphor conversion layer bonded to a fiber optic (FO) bundle taper ④, and a 16 mega pixel CCD camera operating at 1MHz (not shown). As the electron energy and intensity distributions are related to the chemistry on the sample surface; chemical information is represented in the image.

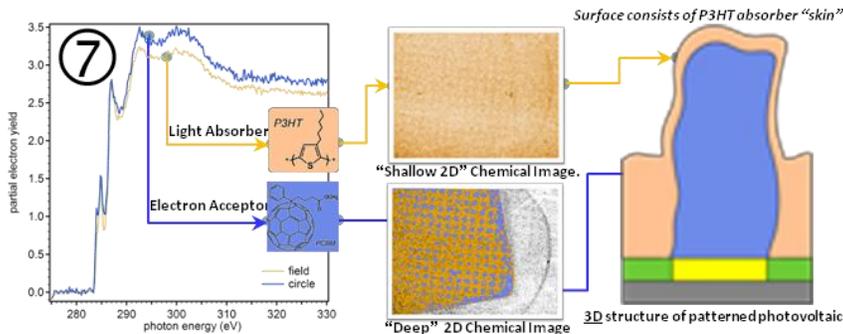


The LARIAT MKII ⑤ employs superconducting magnets with a field at the sample of 9 Tesla and 0.65 Tesla at the detector. Two electrostatic elements, a High Field and a Low Field retarding element, screen both axial energy and angular emission to permit depth and energy dependent filtering. System resolution, throughput and energy-depth discrimination has been improved significantly for LARIAT MKII on NSLS II.

The first application example of the LARIAT confirms successful patterning of single stranded DNA by distinguishing two types of nitrogen chemistry through chemical imaging ⑥ (D. Castner, NESAC/BIO, Univ. of Wash.). The green in the image on the right represents the Adenine π bond of DNA patterned against the nitrogen chemistry of the substrate, shown in red. The analysis not only confirms the successful patterning but discriminates between subtle differences in the two sets of spectra depicted on the left. Another significant aspect of this application example is the integration of the multivariate analysis package AXSIA. This export restricted analytical software developed at Sandia National Laboratory dramatically improves S/N, here reducing a 300 count image stack to one super image. AXSIA employs a proprietary principal component analysis algorithm to mine large spectral data sets for small but relevant spectral variations. AXSIA's continued expansion into diverse scientific disciplines reflects the trend toward hyperspectral and multispectral analytical methods. Optimal scientific methods require cutting edge hardware and software and the LARIAT incorporates custom data acquisition and a sophisticated data reduction tool suite in a complete analytical system.



A second example relates to organic photo voltaic patterning via SAMs templates. NEXAFS chemically distinguishes between the electron acceptor (PCBM) and light absorber (P3HT) chemistries and the LARIAT produces chemical data at varying depth to reveal 3D photovoltaic structural information (D. Delongchamp,



NIST/MSEL) ⑦. The “shallow” chemical image coded in beige shows the surface to consist exclusively of P3HT. The “deep” chemical image coded in blue and beige shows the pattern of PCBM (blue) below the surface in the P3HT matrix. Examined collectively the 3D structural is a pattern consisting of PCBM successfully patterned on the SAMs template and covered with a skin of P3HT.

Micro-calorimeter High-resolution Soft X-ray Detector: Soft x-ray Emission and NEXAFS Spectroscopy

Randy Doriese and Daniel Fischer (NIST)

High-resolution x-ray fluorescence (XRF) spectroscopy, like x-ray photoelectron spectroscopy (XPS), is sensitive to occupied electronic states. A principle difference from XPS, however, is that XRF can probe buried layers from which photoelectrons cannot escape. Such a technique is thus crucial for studying organic photovoltaics, where layer-interface chemistry determines device properties. The few instruments in the world that can perform high-resolution XRF spectroscopy rely on highly inefficient grating spectrometers. Acquisition of useful spectra can take hours or days, even with an undulator beamline, so many classes of experiments, such as spatial scans of nonuniform samples, and observations of time-evolving reactions, are all but ruled out.

The NIST-Boulder Quantum Sensors Project has been collaborating with NIST-Synchrotron Methods Group based at the NSLS since late 2007 to develop a novel x-ray-fluorescence spectrometer that has no wavelength-dispersive element, and is instead based on an array of 256 superconducting transition-edge microcalorimeters. ***When installed at NIST's SST NSLS-II beamline, this instrument will provide spectrometry capabilities – a combination of X-ray energy resolution and measurement speed – that exist nowhere else in the world.***

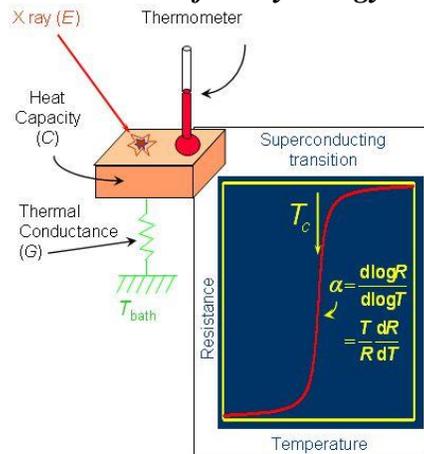
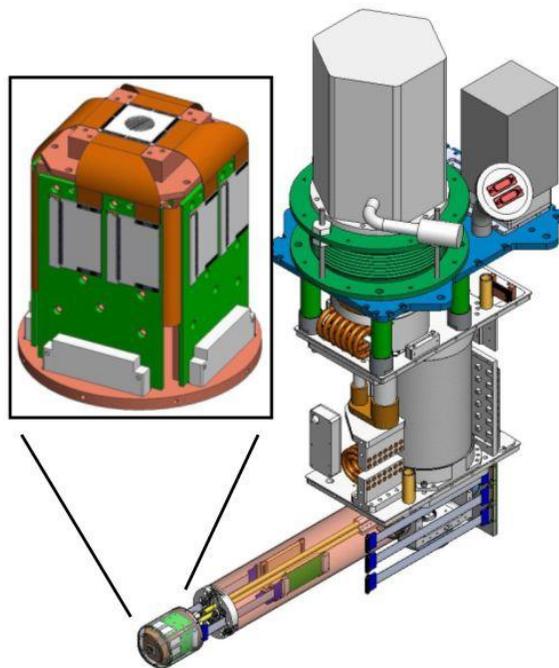


Fig. 1 (Left): TES microcalorimeter. The sharp superconducting transition and low noise due to low-temperature (100 mK) operation allow energy resolution approaching that of grating spectrometers, but with much higher photon efficiency.

A transition-edge-sensor (TES) microcalorimeter is a superconducting thin film that is voltage-biased into its superconducting-to-normal-metal transition. The film is weakly connected to a thermal bath. An x-ray photon striking the film raises its temperature and thus its electrical resistance. The resulting pulsed decrease in electrical current, measured via a SQUID ammeter, has pulse height proportional to the photon energy. Fig. 1 shows a cartoon of a TES.

TESs can be tiled into two-dimensional arrays of hundreds to thousands of pixels. The resulting detector array combines the collecting efficiency of a CCD camera with energy resolution approaching that of a dispersive (crystal or grating) spectrometer. TESs have achieved energy resolution (FWHM) of 22 eV at 100 keV and 1.8 eV at 6 keV. ***In the sub-keV soft-x-ray range, resolution of 0.5 eV in a properly optimized TES should be possible.***

Fig. 2 (right): CAD rendering of the microcalorimeter spectrometer with its vacuum and cryogenic-shield shells removed. The cryogenics consist of a NIST-designed FAA/GGG (50 mK/ 1K) adiabatic demagnetization refrigerator, backed by a Cryomech pulse-tube cryocooler (3 K) in a High Precision Devices cryostat. There will be IR-blocking windows at the 50 mK, 3 K, and 60 K stages with total transmission of about 0.1-1% at 275 eV. The inset shows the 50 mK detector snout. The detector array is on top, and time-division-SQUID-multiplexer chips are arrayed around the sides of the cube.



Our first prototype spectrometer, under development for the NSLS U7A beamline, is optimized for K-alpha fluorescence of carbon and other low-Z elements. ***The design specifications are as follows: 256 pixels, each of size 200 um square, and each capable of receiving up to 100***

x-ray counts per second with energy resolution of 1 eV (FWHM); thus, the total instrument will have collecting area of 10 mm² and count rate of 25 kHz. Fig. 2 shows a CAD rendering of the full instrument.

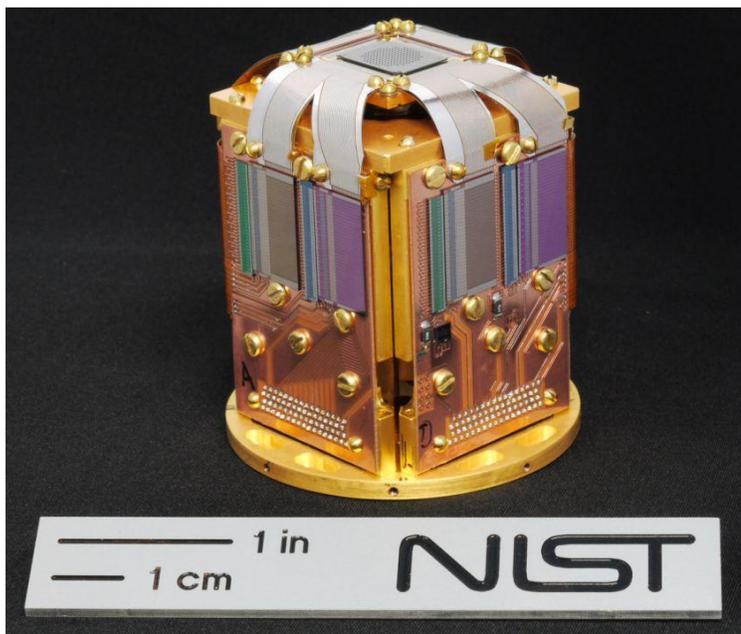
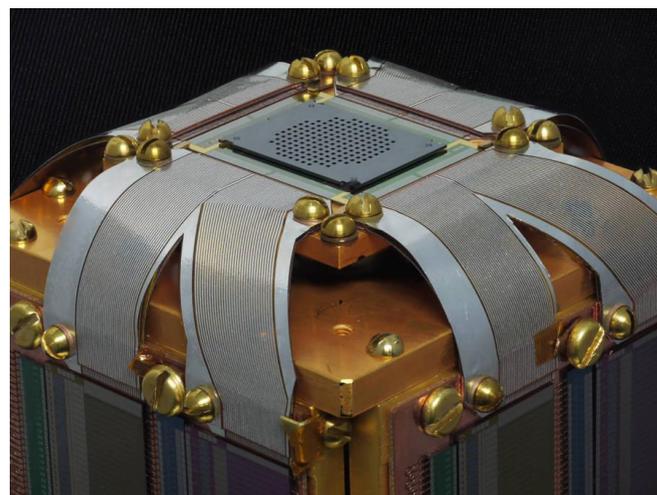


Fig. 3 (left and below): **Photograph of the fully-populated detector snout, which will receive first-light photons from a tube source at NIST-Boulder in June, 2010.**



At U7A, the spectrometer will be stationed in an upstream sample chamber, which will allow the instrument to be deployed for testing, but also to be removed easily from the beamline without impacting the rest of the end stations. This will provide the ideal R&D environment. A CAD rendering of the full system installed into the sample chamber is shown in Fig. 4. This chamber was installed at U7A in May, 2010. Delivery of the instrument is slated for early 2011. We anticipate that by the NSLS / NSLS-II change-over, the microcalorimeter spectrometer will have transitioned from an R&D-grade instrument to a full science instrument that will provide unique spectrometry capabilities to the NSLS-II.

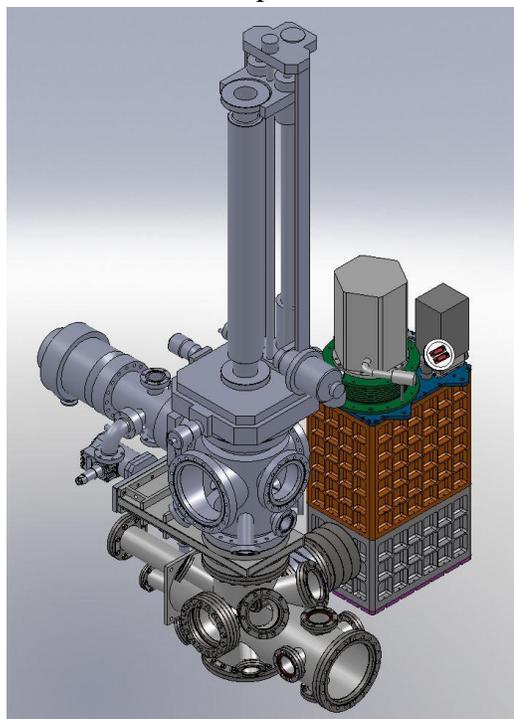


Fig. 4: CAD rendering of the complete microcalorimeter spectrometer installed in its sample chamber.

**NIST's User Community:
25 Academic, 25 Industrial, and 14 National Laboratory Scientific Groups**

Academia	Industry	National Laboratories
ASU	Advanced Materials	Army Research Laboratory
Albany Nano Tech	Aerodyne	BNL, Battery Group
Berkley	Afton Chemical	BNL, Catalysis Group
Clarkson University	Air Products	BNL, Center for Functional Nanomaterials
Cornell	Corning	BNL, Instrumentation Div.
Georgia Tech	Detector Technology	BNL, NSLS Detector Group
Harvard Univ.	Dow Chemical Company	BNL, Superconductivity Group
Hunter College	General Electric	Naval Research Laboratory
Michigan Molecular Institute	H.C. Stark	NIST, Chemical Sciences and Technology Lab.
MIT	IBM	NIST, Electronics and Electrical Engineering Lab.
NCSU, Raleigh	IMEC	NIST, Functional Properties Group
Northeastern Univ.	Int. Radiation Detectors	NIST, Nanomechanical Properties Group
Northwestern Univ.	Konarka	NIST, Polymers Div.
Penn State	Merck	Sandia
Princeton	Motorola	
Stanford Univ.	Ovonic Synthetic Materials	
SUNY Albany	Parc	
SUNY Buffalo	Plextronics	
SUNY Stony Brook	Princeton Gamma Tech	
U. of Delaware	R. Browning Consultants	
U. of Kentucky	SEMATECH	
U. of Penn.	Synchrotron Research, Inc.	
U. of Wash. Seattle	UOP	
UCSB	Xerox	
Yale	X-Lubes	



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June 21, 2010

Ladies and Gentlemen:

The Joint Photon Sciences Institute (JPSI) was established at Brookhaven National Laboratory (BNL) and Stony Brook University (SBU) in the fall of 2008. The mission of JPSI is to exploit the properties of advanced photon sources to address the nation's most critical scientific and technical problems. In particular, JPSI will explore the opportunities offered by the unprecedented brightness of the National Synchrotron Light Source II (NSLS-II).

Specifically, JPSI will create an innovative environment where researchers from universities, industries, and government laboratories can work together to identify major scientific and technological opportunities, create device solutions using the most advanced research tools, and catalyze discovery to deployment. The key element of JPSI's strategy is to leverage the presence of thousands of researchers from the more than 400 companies, universities, and government laboratories that carry out research at the NSLS today and will continue to do so at NSLS-II. In addition, JPSI has formed a strategic alliance with the National Institute of Standards and Technology to promote the usage of synchrotrons by industry.

So far, JPSI has focused its program on four themes: microelectronics, energy storage, extreme environments, and solar energy. In each area, leaders from universities, government laboratories and industries were invited to a focused workshop where major technology challenges and capabilities of advanced research tools were presented, new scientific opportunities identified, and collaborative teams formed. These activities have led to major funding from New York State in energy storage, beamline upgrades at the NSLS for microelectronics research, and a new beamline proposal at the NSLS and NSLS-II for advanced lithography. In parallel, JPSI has launched basic research programs in coherent diffraction imaging and nano-diffraction.

As the Directors of JPSI, we are writing in support of the NIST Spectroscopy Beamline Suite: Soft and Tender X-ray Spectroscopy and Microscopy (100 eV to 7.5 keV canted sources), and Hard X-ray Absorption Spectroscopy and Diffraction (4.5 keV to 40 keV three-pole wiggler source) beamline proposal. The proposed beamline is part of the suite of scientific capabilities identified in the four major workshops. It is the intention of JPSI to engage NSLS-II in a partnership agreement to develop these capabilities and to share the stewardship of these beamlines. The aim is to maximize their impact by engaging the intellectual expertise within JPSI and its research partners in these techniques, and to continue to expand these successful research programs at the NSLS today and NSLS-II tomorrow.

Sincerely yours,



Chi-Chang Kao, Director

John B. Parise, Co-Director

Daniel A. Fischer

Education: 1984 Physics Ph.D. SUNY, Stony Brook

Professional Employment:

Group Leader (2003-present) Synchrotron Methods, Physicist (1991-present):

Ceramics Division, Material Science and Engineering Laboratory,
National Institute of Standards and Technology

Physicist: Exxon Research and Engineering Co., 1984-1991.

Post Doctoral Research Associate: City University of New York, 1984.

Awards:

- *2005 Arthur S. Flemming Award (Scientific Category)*, for pioneering work in developing a critical facility for soft X-ray absorption spectroscopy that has enabled key scientific and technological advances in cutting-edge technology and for groundbreaking work on self-assembled nanoparticles, nanotubes, biomaterials, and high-temperature superconductors.
- *2004 Department of Commerce Gold Medal, Individual Award*, for pioneering development of a unique national measurement facility for soft x-ray absorption spectroscopy enabling breakthrough materials advances.
- *1998 Department of Commerce Bronze Medal, Group Award*, for leadership and scientific achievement in the development, implementation, and application of advanced x-ray techniques for materials science.
- *1994 Department of Commerce Bronze Medal, Individual Award*, for the development of ultra-soft x-ray techniques to measure molecular structure at surfaces and buried interfaces.

Selected Recent Service to the Scientific Community:

2005-2008: Chair and Vice Chair National Synchrotron Light Source User Executive Committee

2006: NSLS User meeting Chair (over 400 attendees, 3 days, 9 workshops)

2006-present: Editorial Board Member- Review of Scientific Instruments

1998-present: Chair NSLS Vacuum Ultraviolet Proposal Study Panel

2007-present: Member NSLS to NSLS II Beamline Transition Working Group

Over 250 Journal Publications

(Below some selected publications; *Journal Covers and ⁺NSLS Science Highlights)

*⁺ "Enhanced Photovoltaic Properties of Potassium-Adsorbed Titania Nanotubes", C Richter, C Jaye, D Fischer, L Lewis, R Willey, L Menon, J. Mater. Chem., 19, 2963–2967 (2009).

⁺ "Influence of Dielectric Surface Chemistry on the Microstructure and Carrier Mobility of an n-Type Organic Semiconductor", P Dhagat, H Haverinen, J Klein, Y Jung, D Fischer, D Delongchamp, G Jabbour, Adv. Func. Mater., 19, 2365-2372 (2009).

⁺ "Enhancement of Engine Oil Wear and Friction Control Performance Through Titanium Additive Chemistry", J Guevremont, G Guinther, D Szemenyei, M Devlin, T Jao, C Jaye, J Woicik, D Fischer, Tribol. Trans., 51(3), 324-331 (2008). (*Selected for Editor's Choice Award*)

* "Multilayer mirror fluorescence detection system for photon-in photon-out in-situ carbon K-edge NEXAFS", D Fischer, S Sambasivan, A Kuperman, Y Platonov, J Wood, Synch. Rad. News, 15, 16-20 (2002).

Name: Joseph C. Woicik

Education/Training:

Institution and Location	Degree	Year	Field of Study
Stanford University, Stanford CA	Ph.D. and M.S.	1989	Applied Physics
Stanford University, Stanford CA	M.S.	1989	Applied Physics
Cornell University, Ithaca NY	B.S.	1983	Applied Physics

Research and Professional Experience:

National Institute of Standards and Technology

Senior Physicist	1999-present
Physicist	1991-1999
National Research Council Post Doctoral Fellow	1989-1991

Professional Activities:

Spokesperson, beamline X2A2 NSLS

Local contact, beamline X24A NSLS

Staff member, APS Sector 33, 2002-2004

Chair, International Workshop for New Opportunities in Hard X-ray Photoelectron Spectroscopy: HAXPES 2009, Brookhaven National Laboratory, 5/20/09 – 5/22/09.

Chair, Advanced Photon Source Spectroscopy Review Panel, 2003-2005

Recent Awards:

Department of Commerce Bronze Metal	1998
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Selected Publications:

1. Performance of a 4-element Si drift detector for x-ray absorption fine-structure spectroscopy: Resolution, maximum count rate, dead-time correction, and incorporation into the Athena data analysis software, J.C. Woicik, B. Ravel, D.A. Fischer, and W.J. Newburgh, *J. Synch. Rad.* **17**, 409 (2010).
- 2*. Oxygen vacancies in N doped anatase TiO₂: Experiment and first-principles calculations, A.K. Rumaiz, J.C. Woicik, E. Cockayne, H.Y. Lin, G.H. Jaffari, and S.I. Shah, *Appl. Phys. Lett.* **95**, 262111 (2009).
- 3** .A ferroelectric oxide made directly on silicon, M.P. Warusawithana, C. Cen, C.R. Slesman, J.C. Woicik, Y. Li, L.F. Kourkoutis, J.A. Klug, H. Li, P. Ryan, L.-P. Wang, M. Bedzyk, D.A. Muller, L.-Q. Chen, J. Levy, and D.G. Schlom, *Science* **324**, 367 (2009).
- 4*. Phase identification of self-forming Cu-Mn based diffusion barriers on p-SiOC:H and SiO₂ dielectrics using x-ray absorption fine structure, J.M. Ablett, J.C. Woicik, Zs. Tokei, S. List, and E. Dimasi, *Appl. Phys. Lett.* **94**, 042112 (2009).
5. Strain-induced change in local structure and its effect on the ferromagnetic properties of La_{0.5}Sr_{0.5}CoO₃ thin films, C.K. Xie, J.I. Budnick, W.A. Hines, B.O. Wells, and J.C. Woicik, *Appl. Phys. Lett.* **93**, 182507 (2008).
6. Ferroelectric distortion in SrTiO₃ thin films on Si(001) by x-ray absorption fine structure spectroscopy: Experiment and first-principles calculations, J.C. Woicik, E.L. Shirley, C.S. Hellberg, K.E. Andersen, S. Sambasivan, D.A. Fischer, B.D. Chapman, E.A. Stern, P. Ryan, D.L. Ederer, and H. Li, *Phys. Rev. B* **75**, Rapid Communications, 140103 (2007).
7. Site-specific valence x-ray photoelectron spectroscopy, J.C. Woicik, *Synchrotron Radiation News* **17**, 48 (2004).
- 8*. Hybridization and bond-orbital components in site-specific x-ray photoelectron spectra of rutile TiO₂, J.C. Woicik, E.J. Nelson, L. Kronik, M. Jain, J.R. Chelikowsky, D. Heskett, L.E. Berman, and G.S. Herman, *Phys. Rev. Lett.* **89**, 077401 (2002).
9. Direct measurement of valence-charge asymmetry by x-ray standing waves, J.C. Woicik, E.J. Nelson, and P. Pianetta, *Phys. Rev. Lett.* **84**, 773 (2000).
- 10*. Bond-length distortions in strained-semiconductor alloys, J.C. Woicik, J.G. Pellegrino, B. Steiner, K.E. Miyano, S.G. Bompadre, L.B. Sorensen, T.-L. Lee, and S. Khalid, *Phys. Rev. Lett.* **79**, 5026 (1997).
11. Diffraction anomalous fine structure: A new x-ray structural technique, H. Stragier, J.O. Cross, J.J. Rehr, Larry B. Sorensen, C.E. Bouldin, and J.C. Woicik, *Phys. Rev. Lett.* **23**, 3064 (1992).
12. Studies of Si - Ge interfaces with Surface EXAFS and photoemission, J.C. Woicik and P. Pianetta, in Synchrotron Radiation Research: Advances in Surface and Interface Science: Issues and Technology, Ed. R.Z. Bachrach, 1992 Plenum Press, New York.

* NSLS/BNL Highlight

** APS/ANL Highlight

Name: Bruce Ravel

Education/Training:

Institution and Location	Degree	Year	Field of Study
University of Washington	Ph.D	1997	Physics
Wesleyan University	B.A.	1989	Physics (<i>magna cum laude</i>)

Research and Professional Experience:

<u>National Institute of Standards and Technology</u>	Scientist, Synchrotron Measurement Group	Nov. 2007-present
	National Research Council Postdoctoral Fellow	1997-1999
<u>Argonne National Laboratory</u>	Physicist, Biology Division	2005-2007
<u>Naval Research Laboratory</u>	Physicist, Chemistry Division	2001-2005
<u>Centre Nationale de la Recherche Scientifique</u>	Visiting scientist	2000-2001

Professional Activities:

- Beamline experience
 - Local contact, beamline X23A2 2007-present
 - Staff member, APS Sector 10, 2005-2007
 - Spokesperson, beamlines X11A, X11B, X23B, 2003-2005
- Committees
 - Executive committee member, International X-ray Absorption Society, 2005-present
 - Chair, NSLS User Executive Committee, 2009-2010
- XAS software and education
 - Organizer/instructor XAS Schools: NSLS (2003-2005, 2008, 2009), APS (2006-2009), SLS (2007,2009), Thai Synchrotron (2009,2010), University of Alberta (2005), Polish Academy of Science (2006), University of Ghent (2010)
 - Co-author of the IFEFFIT package, a widely used package for XAS data analysis, 2001-present
 - Contributing author of FEFF8, a widely used XAS theory program
- Review Panels
 - Proposal Review Panel, National Synchrotron Light Source, 2007-present
 - Proposal Review Panel, Advanced Photon Source, 2006-present
 - Proposal Review Panel, Canadian Light Source, 2006-present

Selected Publications:

1. *ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT*, B. Ravel and M. Newville, *J. Synchrotron Rad.* **12**, pp. 537-541 (2005), [doi:10.1107/S0909049505012719](https://doi.org/10.1107/S0909049505012719)
At 706 citations, this is the most frequently cited article from The Journal of Synchrotron Radiation.
2. *Real Space Multiple Scattering Calculation and Interpretation of X-Ray Absorption Near Edge Structure*, A.L. Ankudinov, B. Ravel, J.J. Rehr, and S. Conradson, *Phys. Rev* **B58**, #12, pp. 7565-7576, (1998), [doi: 10.1103/PhysRevB.58.7565](https://doi.org/10.1103/PhysRevB.58.7565)
3. *Simultaneous XAFS measurements of multiple samples*, B. Ravel, C. Scorzato, D.P. Siddons, S.D. Kelly, S.R. Bare, J. Synchrotron Radiat., **17** (2010) 380-385, [doi:10.1107/S0909049510006230](https://doi.org/10.1107/S0909049510006230)
4. *Performance of a four-element Si drift detector for X-ray absorption fine-structure spectroscopy: resolution, maximum count rate, and dead-time correction with incorporation into the ATHENA data analysis software*, J.C. Woicik, B. Ravel, D.A. Fischer, W.J. Newburgh, J. Synchrotron Radiat., **17** (2010) 409-413, [doi:10.1107/S0909049510009064](https://doi.org/10.1107/S0909049510009064)
5. *The structure of ion beam amorphised zirconolite studied by grazing angle X-ray absorption spectroscopy*, D.P. Reid, M.C. Stennett, B. Ravel, J.C. Woicik, N. Peng, E.R. Maddrell and N.C. Hyatt, *Nuclear Instruments and Methods in Physics Research B* **268**:11-12, (2010) 1847-18521, [doi:10.1016/j.nimb.2010.02.026](https://doi.org/10.1016/j.nimb.2010.02.026)
6. *Condensed Matter Astrophysics: A Prescription for Determining the Species-specific Composition and Quantity of Interstellar Dust Using X-rays*, J.C. Lee, J. Xiang, B. Ravel, J. Kortright K. Flanagan, *The Astrophysical Journal* **702**:2 (2009) 970, [doi: 10.1088/0004-637X/702/2/970](https://doi.org/10.1088/0004-637X/702/2/970)
7. *Protein Oxidation Implicated as the Primary Determinant of Bacterial Radioresistance* M. J. Daly, E. K. Gaidamakova, V. Y. Matrosova, A. Vasilenko, M. Zhai, R. D. Leapman, B. Lai, B. Ravel, S.-M. W. Li, K. M. Kemner, J. K. Fredrickson *PLOS Biology* **5**:4, (2007), [doi:10.1371/journal.pbio.0050092](https://doi.org/10.1371/journal.pbio.0050092)