Actinides and Rare Earths Focus Topic
Room 22 - Session AC+Ml+SA-SU-MoM

Magnetism, Complexity, and Superconductivity in the Actinides and Rare Earths

Moderator: Tomasz Durakiewicz, Los Alamos National Laboratory

8:20am AC+Ml+SA+SU-MoM-1 Magnetic and Transport Characteristics in the Uranium Intermetallic Compounds with the HoCoGa3-type Structure, Yoshinori Haga, Japan Atomic Energy Agency, Japan INVITED

Physical properties of actinides compounds are mainly dominated by the 5f electrons behavior. The spatial extent of the 5f wave function and resulting hybridization with the neighboring atoms lead to itinerant characters. On the other hand, well isolated 5f electrons carry magnetic moment. Competition between those two characteristics often bring about peculiar electronic properties. Among a series of actinides compounds, so-called 115 compounds crystallizing in the tetragonal HoCoGa3-type structure have extensively been object of unusual correlated electronic states, including heavy effective mass of conduction electrons, magnetic ordering and heavy fermion superconductivity. Those compounds are also good cases to study electronic transport properties in detail because of availability of extremely high quality samples. Among them, we discuss electronic properties of URhIn3 (X = Ga and In). While URhIn3 orders antiferromagnetically at fairly high temperature 98 K, isostuctural and formally isoelectronic analogue URhGa3 is a nonmagnetic semimetal[1,2,3]. Detailed transport measurements as well as the de Haas-van Alphen experiment revealed Fermi surface characteristics. We discuss origin of magnetism of uranium 5f electrons and its relationship between superconductivity realized in Pu-analogues.


9:00am AC+Ml+SA+SU-MoM-3 Magnetic Structures of Layered U,RhIn3 materials, Attila Bartha, M Klipera, Charles University, Prague, Czech Republic; P Čermák, Forschungszentrum Juelich GmbH, Germany; B Ouladiff, Institut Laue Langevin, France; P Javorsky, J Custers, Charles University, Prague, Czech Republic

Materials of reduced dimensionality appear in many contemporary fields of research and technology, because they encompass a wide variety of interesting electronic phenomena. For instance carbon can be prepared in 3D (diamond), quasi-2D (graphite), 2D (graphene) or 1D (carbon nanotubes). All of these structures have distinct electronic properties. Diamond is an insulator. Graphene is semimetal. However, when the dimensionality is increased by putting several graphene layers together (eventually making graphite), the resulting band structure moves to that of a more trivial graphite. Another example is high temperature superconductors being quasi-2D as well.

The role of dimensionality in f-electron systems has been mainly discussed in the context of quantum phase transitions and related phenomena. The series of CuInxTm1-x(Tm = In, Ga) family of compounds. Neutron diffraction measurements were performed on structurally well-defined single crystals. Both, URhIn3 and U2RhIn8, adopt the tetragonal HoCoGa3-type structure (P4/mmm) typical for this group of compounds. URhIn3 orders antiferromagnetically below T = 98 K. The magnetic propagation vector equals k = (0.5, 0.5, 0) and we obtained a value of 1.65 μU⊥ for the size of the ordered magnetic moment. The antiferromagnetic transition temperature of U2RhIn8 is higher yielding 117 K. We found that the magnetic structure can be described by propagation vector k = (0.5, 0.5, 0). The respective ordered magnetic moment amounts 1.7 μU⊥. In both materials the ordered magnetic moments are aligned along the tetragonal c-axis. Comparison with isostructural compounds and general conclusions for the series will be presented.


9:20am AC+Ml+SA+SU-MoM-4 U3Si2 — Physical Properties and Resistance to Hydrogen, Silvie Maskova, Charles University, Prague, Czech Republic; K Miliyanchuk, Ivan Franko National University of Lviv, Lviv, Ukraine; S Middleton, Westinghouse Electric Sweden AB, Vasteras, Sweden; L Havela, Charles University, Prague, Czech Republic

U3Si2 (tetragonal structure with the space group of Pa3mmb and two different U-positions, U1 and U2, in the unit cell) is considered to be promising material (due to its high density of uranium) as an accident-tolerant nuclear fuel [1] with rather high melting point (1938 K) indicating a high thermodynamic stability. From this point of view, it is very important to study its resistance to oxygen or hydrogen, as it can significantly influence the integrity of the material. U3Si2 was reported to oxidize at elevated temperatures [2].

We studied the H absorption and concomitant changes of basic electronic properties. We found that U3Si2 reversibly absorbs hydrogen (H can be released again by heating up to approx. 700 K) to the level of approximately 1.8 H/f.u., i.e. yielding U3Si2Hx. The H absorption proceeds at very low H pressures (kPa range) already, resulting in 10% volume expansion. The temperature-induced desorption experiment showed that the hydrogen atoms are located in one specific position only. The crystal structure arrangement suggests that two different positions should be considered - U3Si2 tetrahedra (similar to UiX tetrahedra in Ui2X compounds [3] crystallizing in an ordered ternary derivative of the U3Si2 structure) and a split position in the Ui octahedra consisting of 4 Ui and 2 U atoms (H atom shifts from the central position into the tetrahedra formed by 2 Ui and 2 U atoms. As H generally does not occupy two adjacent tetrahedra, we can assume only two from the 4 tetrahedra occupied). The latter was confirmed as more plausible option by ab-initio calculations using Vienna Ab-initio Simulation Package (VASP) with the PBE-GGA exchange correlation.

Magnetic studies of U3Si2 confirmed that it is a Pauli paramagnet, as reported previously [4]. The volume expanded hydride reveals a Curie-Weiss behavior and a weak and inhomogeneous ferromagnetism arising gradually below T = 100 K. The low-temperature specific heat of U3Si2Hx shows an upturn and a dramatic enhancement of the Sommerfeld coefficient of electronic specific heat γ, which reaches 440 mJ/mol f.u. K 2 (γ = 88 mJ/mol f.u. K 2 for U3Si2).

This work was supported by The Czech Science Foundation under the Grant No. 15-11005.


9:40am AC+Ml+SA+SU-MoM-5 Understanding Surface Chemistry of f-element Oxides Using First-principle Methods, Ping Yang, Los Alamos National Laboratory INVITED

Interfacial chemistry for f-element materials is critical for nuclear waste management and to address the environmental concerns associated with actinides. Cerium is often used as a surrogate for more radioactive actinide elements for thorough characterization using advanced spectroscopic techniques. Herein, we will present recent progress in characterizing interfacial interactions of ligands with CeO2 and ThO2 in both surface and nanoparticle forms. We will demonstrate how the synergy between theory and experiment has accelerated the progress in this field. The theoretical results are validated by spectroscopic characterizations. A better molecular-level understanding of the interfacial chemistry including coordination, energetics and reaction mechanisms will pave the way to a better strategy for waste management and environment remediation.
The energy-wavevector dispersion relations for normal modes of vibration propagating along high-symmetry lines in NpO$_2$ and UO$_2$ have been determined by measuring the coherent one-phonon scattering of X-rays from single-crystal specimens with mass varying from a few μg to ~1 mg. The inelastic X-ray scattering (IXS) experiments were carried out using the ID28 beamline at ESRF with an incident energy $E=17.794$ keV. The results are compared against $ab initio$ phonon dispersion simulations computed within the first-principles density functional theory in the generalized gradient approximation plus Hubbard $U$ correlation (GGA+$U$) approach, taking into account third-order anharmonicity effects in the quasiharmonic approximation.

In the case of NpO$_2$, the sample of dimension of $0.4\times0.3\times0.3\text{mm}^3$ was oriented with the specular direction along the (100) crystal axis and the (011) axis in the scattering plane. We have investigated different Brillouin zones in order to optimize the inelastic structure factor for the different optic branches. Optic phonons arise mainly from oxygen vibration modes and are very weak. Thermal expansion, heat capacity, thermal conductivity, phonon linewidth, and thermal phonon softening are calculated and compared with experimental data available for both NpO$_2$ and UO$_2$ [1]. We show that optical phonons contribute significantly to the heat transport due mainly to their large velocities and short lifetimes. Compared with UO$_2$, the main differences in the phonon density of states of NpO$_2$ are a softening of the optical modes and an increase of the peak centred around 55 meV, whereas the acoustic modes in NpO$_2$ are shifted to higher frequencies. The calculated value at 0 K of the bulk modulus in NpO$_2$ is in agreement with the experimental value and slightly smaller than the one determined by high-pressure X-ray diffraction for UO$_2$. NpO$_2$ has a smaller thermal conductivity than UO$_2$, at least in the temperature range 600 to 1000 K for which experimental values are available.

The lattice dynamics of UO$_2$ have been extensively investigated by neutron scattering both at low and high temperature. In this study we focussed our attention to the low temperature region, searching for vibronic contributions to the vibrational-magnetic-quadrupolar mixed modes that appear in UO$_2$ because of magnetoelastic and multipolar superexchange interactions. The situation is cleaner than with neutrons, as the latter see both magnons and phonons – the IXS spectra just the phonons. This observation opens a new window on these “hidden excitations”, which drive much of the physics of UO$_2$.

Actinides and Rare Earths Focus Topic
Room 22 - Session AC+AS+SA+SU-MoA

Chemistry and Physics of the Actinides and Rare Earths
Moderator: David Shuh, Lawrence Berkeley National Laboratory

1:40pm AC+AS+SA+SU-MoA-1 Oxidation and Crystal Field Effects in Uranium, James G. Tobin, University of Wisconsin-Oshkosh; S Yu, Lawrence Livermore National Laboratory; C Booth, Lawrence Berkeley National Laboratory; T Tyliszczak, Lawrence Berkeley Lab, University of California, Berkeley; D Shuh, Lawrence Berkeley National Laboratory; G van der Laan, Diamond Light Source, UK; D Sokaras, D Nordlund, T Weng, Stanford Synchrotron Radiation Lightsource; P Bagus, University of North Texas
An extensive investigation of oxidation in uranium has been pursued. [1] This contribution presents the observation of soft X-ray absorption spectroscopy, hard-x-ray absorption near-edge structure, resonant (hard) x-ray emission spectroscopy, cluster calculations, and a branching ratio analysis founded on atomic theory. The samples utilized were uranium dioxide (UO$_2$), uranium trioxide (UO$_3$), and uranium tetrfluoride (UF$_4$). A discussion of the role of nonspherical perturbations, i.e., crystal or ligand field effects, will be presented. The conclusions are as follows. (1) The hypothesis of the potential importance of CF effects in the XAS branching ratio (BR) analysis of 5f states was incorrect. (2) Both UO$_2$ and UF$_4$ are n$_F$ = 2 materials. The combination of the 4d XAS BR and RXES analysis is particularly powerful. (3) CF broadening in the L$_3$ RXES spectroscopy does not preclude a successful analysis. (4) The prior experimental result that n$_F$(UO$_3$) = 3 and the proposed causation by covalent bonding was incorrect. UO$_3$ is an n$_F$ = 2 material and analysis within a simple, ionically localized picture provides the correct result. (5) UO$_2$ appears to be an n$_F$ = 1 material. (6) While the 4d XAS BR analysis is blind to CF effects, crystal field and covalence remain important. (7) For localized actinide systems, the 4d XAS BR analysis founded upon the utilization of the intermediate coupling scheme remains a powerful tool. (8) For delocalized actinide systems, the BR analysis is problematic.[1] J. G. Tobin, S.-W. Yu, C. H. Booth, T. Tyliszczak, D. K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng, and P. S. Bagus, Phys. Rev. B 92, 035111 (2015)

2:00pm AC+AS+SA+SU-MoA-2 Electron Spectroscopy Studies of U and U-Mo Hydrides, Ladislav Havela, M Paukov, M Dopita, L Horak, M Divis, I Turek, Charles University, Prague, Czech Republic; T Gouder, A Seibert, F Huber, European Commission, Joint Research Centre, Karlsruhe, Germany; D Legut, VSB - Technical University of Ostrava, Czech Republic
U hydride was the first material indicating that 5f states can yield ferromagnetism analogous to 3d metals. However, the electronic structure of UH$_3$ is not yet well understood, and it is not clear to which extent it can be described by conventional band structure calculations. We have been studying structure and electronic properties of UH$_3$ and (UH$_3$)$_x$Mo$_y$ films, synthesized by reactive sputtering. Primary diagnostics was performed by in-situ XPS. The U-4f core level spectra exhibit a development as a function of partial pressure of H$_2$ in Ar (p$_{H_2}$ = 8*10$^{-3}$ mbar). Their intensity gradually decreases, they shift by 0.2 eV towards higher binding energies (BE) and an extended (9 eV wide) satellite structure develops on the high BE side of both 4f peaks. This tendency saturates at 5% H$_2$ concentration, and we assume that this pressure is sufficient to form UH$_x$. XRD and X-ray reflectivity proved indeed the β-UH$_3$ structure of deposited films, which were polycrystalline, but highly textured. Ferromagnetism of the UH$_3$-based hydrides, we believe, is a powerful tool. (8) For delocalized actinide systems, the 4d XAS BR analysis is blind to CF effects, crystal field and covalence remain important. (7) For localized actinide systems, the 4d XAS BR analysis founded upon the utilization of the intermediate coupling scheme remains a powerful tool. (8) For delocalized actinide systems, the BR analysis is problematic.

Monday Afternoon, October 30, 2017

2:20pm AC+AS+SA+SU-MoA-3 Comparative Structural Studies of Tetravalent f Ions in Solids and in Aqueous Solutions, Lynda Soderholm, Argonne National Laboratory
INVITED
Predicting a metal ion’s aqueous chemistry – including its stability, reactivity, and solubility – requires molecular-level knowledge of the various factors influencing speciation and complex formation. This chemistry is particularly complicated for f-ions, where the electrostatic, non-directional bonding provides flexibility to their coordination environments, which can vary widely depending on the ligating species. This presentation will focus on our efforts to establish trends in f-ion solution behavior and to provide a direct link between metal correlations in solution and the thermodynamic stability constants that are used to derive relative free energies of available metal-ligand complexes. Although several examples will be provided, the discussion will center on a comparison between the behaviors of tetravalent Th, Pu, and Ce and how differences in the complexes formed in solution impact the composition and structure of precipitates that form. High-energy X-ray scattering (HEXS) experimental results will be used to demonstrate how changing conditions can influence solution chemistry, with a specific emphasis on the role of the anion. X-ray surface-based techniques will be used to provide a link between solution speciation and the complexes that form on mineral surfaces. The structures of molecular species isolated as single-crystals from these solutions will be directly compared with the solution and surface-adsorbed species. This work is supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, Heavy Element Chemistry, under contract No. DE-AC02–06CH11357.

4:00pm AC+AS+SA+SU-MoA-8 Interfacial Dynamics in Radiation Environments and Materials: An Energy Frontier Research Center, Sue Clark, Pacific Northwest National Laboratory
INVITED
The US Department of Energy’s Office of Environmental Management (EM) is faced with remediating millions of liters of highly radioactive wastes that resulted from the production of nuclear weapons during the Cold War. These legacy wastes are stored in large, underground tanks at former nuclear weapons production sites in the US. Not only are these wastes radioactive, but they are also highly alkaline and concentrated in electrolytes. Using currently available technologies and approaches, EM estimates that processing these wastes into disposal forms in a geologic repository will take at least 5 decades and over $300 billion dollars. Basic research on the chemical and physical behavior of these materials in such extreme conditions is needed to provide a foundation of innovation to accelerate processing and reduce aggregate costs. IDREAM is an Energy Frontier Research Center (EFRC) conducting fundamental research to support innovations in processing high-level radioactive wastes (HLW). Activities in IDREAM are designed to support the transformation of HLW processing by elucidating the basic chemistry and physics required to control and manipulate interfacial phenomena in extreme HLW environments (e.g., non-equilibrium, heterogeneous, and chemically-complex). This foundational knowledge is required to achieve IDREAM’s vision to master molecular–to–mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing (g,b) radiation. Further, understanding these processes will enable prediction of waste aging over the many decades required to complete this difficult cleanup task. Currently, IDREAM activities focus on the aluminate anion in alkaline solutions, and its nucleation into boehmite (aluminum (oxy)hydroxide, AlO(OH)) and gibbsite (aluminum hydroxide, Al(OH)$_3$), as they are key principal components of bulk waste materials to which a variety of other metal ions and radionuclides partition. In this presentation, initial results on interfacial reactivity between aluminate, boehmite, and gibbsite will be discussed. The impact of g and b radiation on boehmite and gibbsite will also be presented.

4:40pm AC+AS+SA+SU-MoA-10 Real Structure of Nanocrystalline Uranium based Hydrides Studied By the X-ray Scattering Methods, Milan Dopita, L Havela, L Horak, M Paukov, Charles University, Prague, Czech Republic; Z Matej, MAX-L, Lund, Sweden
Interaction of hydrogen with uranium is not only an important issue for its nuclear and military applications but also contributes to understanding of
the $5f$ magnetism. Uranium hydrides provide a unique tool to observe an impact of expansion of the U lattice, allowing formation of U moments and their ferromagnetic ordering. However, the electronic structure of uranium hydrides is not fully understood yet. Especially, the role of the real structure, i.e. the influence of the lattice defects, particle size in the nanocrystalline bulk materials and the preferred orientation of crystallites – the texture, the strains and stresses in the case of films is not well described explicitly, but can significantly influence electronic and magnetic properties of materials.

In our contribution we report the real structure of bulk and powder Mo and Zr-alloyed uranium hydrides, prepared by rapid (splat) cooling and high pressure synthesis, and Mo alloyed uranium hydride films synthesized by reactive sputtering, using X-ray scattering methods. The sample series with different alloying element concentration as well as at different hydrogen pressure were prepared. Since the classical powder diffraction methods, as the profile analysis and/or Rietveld method, reach the limits of their applicability for the nanocrystalline uranium hydrides allows in terms of the real structure description, the use of more advanced methods is necessary.

Here we describe the total scattering method – pair distribution function analysis, and Debye equation calculation for simulations of the intensity scattered from nanocrystalline clusters.

The key results of our study were the determination of the phase composition and its evolution, as well as detailed atomic positions, which can influence the U-U spacings in individual phases, tuning the $5f$ magnetism. The methods are able to describe the particle size and defect distributions, the stress, strains, and textures in the films. In addition, the depth profiles and evolution of above mentioned parameters can be determined. Such X-ray analysis provides useful characterization of the sputter-deposited films, which are also used for fundamental electron spectroscopy studies of UH$_3$-based films, exhibiting much lower surface contamination by oxygen than comparable bulk material.

This work was supported by the project "Nanomaterials centre for advanced applications", Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

### Magnetic Interfaces and Nanostructures Division

**Room 11 - Session MI+B1+EM+SA-MoA**

#### Role of Chirality in Spin Transport and Magnetism

**Moderators:** Greg Szulczewski, The University of Alabama, Hendrik Ohldag, SLAC National Accelerator Laboratory

**1:40pm MI+B1+EM+SA-MoA-1 Spin Transport and Polarization in Chiral Molecules: Theory and Possible Applications, Karen Michaeli, Weizmann Institute of Science, Israel**

The functionality of many biological systems depends on reliable electron transfer. Unlike artificial electric circuits, electron transport in nature is realized via insulating chiral (i.e., parity-symmetry breaking) molecules. Recent experiments have revealed that transport through such molecules strongly depends on the electron’s spin relative to the propagation direction. In the talk I will introduce the mechanism behind this phenomenon, which has been dubbed chiral induced spin selectivity (CISS). The discovery of the CISS effect has raised important questions about the role of spin in biological processes more generally, and suggests the possibility of a new class of organic-based nanoscale devices. I will discuss some of the key developments regarding spin selectivity; I will present new questions that arise from these results and offer ideas for their resolution.

**2:20pm MI+B1+EM+SA-MoA-3 Enantio-sensitive Charge Transfer in Adsorbed Chiral Molecules Probed with X Ray Circular Dichroism, F Luque, Universidad Autónoma de Madrid, Spain; I Kowalk, Polish Academy of Sciences, Poland; M Niño, IMDEA-Nanoscience, Spain; D Arvanitis, Uppsala University, Sweden; Juan José de Miguel, Universidad Autónoma de Madrid, Spain**

Recent studies have shown how layers of purely organic, chiral molecules can induce the appearance of strong spin polarization in initially unpolarized electron currents: [1] Furthermore, spin-polarized photoemission experiments comparing adsorbed films of opposite enantiomers of the same chiral molecule have revealed that they can display different behavior, producing spin polarization along different directions in space instead of simply changing its sign. [2]

In this study enantio-pure ultrathin films of chiral 1,2-diphenyl-1,2-ethanediol (DPED) have been deposited on Cu(100) at 100 K and studied at the MAX-lab synchrotron in Lund, Sweden, using circularly polarized x-ray absorption (XAS) at the carbon K edge. XAS excites element-specific core electrons to empty levels in the ground state thus probing the molecule’s electronic configuration. The different features present in the absorption spectra have been identified and assigned to specific electronic transitions.

The comparison of absorption spectra taken with photons of opposite helicity shows a surprisingly strong dichroism localized at transitions into empty d- or f-orbitals of the molecule. The mirror image of the spectra reveals that this response is associated to the charge transferred between the Cu substrate and the adsorbed molecules. This charge is found to be polarized in orbital momentum, and the direction of the polarization is different for the two enantiomers studied: (R,R)–DPED and (S,S)–DPED. These findings indicate that chiral organic layers can play an important role in the emerging field of molecular orbitronics.


**Monday Afternoon, October 30, 2017**
Monday Afternoon, October 30, 2017


We report results from an electron spin resonance (ESR) study to probe the spin-dynamics in the conducting polymer poly[(N, N-bis(2-octyldodecyl)-naphtalene-1,4,5,8-bis(dicarboximide)-2,6-diy]-alt-5,5’-9,9’-(2,2’-bithiophene)] or PNDI2OD-T2. Chemical reduction of the polymer was achieved by using cobaltacene, which introduces unpaired electrons into the polymer. Continuous wave ESR measurements were done on frozen solutions and thin films over the temperature range of 77 to 300 K. Narrow ESR peaks with broad tails were observed, suggesting strong one-dimensional anisotropic conduction. Electron nuclear double resonance spectroscopy was used to analyze the hyperfine coupling of the frozen solutions. The results indicate a proton hyperfine coupling of 1.5 MHz, which suggests the spins are delocalized over several monomer units. Electron spin echo envelope modulation spectroscopy was measured from 6 to 90 K to investigate the spatial distribution of nuclear spins in the environment of the unpaired electrons spins. The measurements show that spin relaxation increases rapidly when the temperature in increases from 6 to 90 K. A kinetic model that accounts for the spin-dynamics will be presented.

4:00pm MI+Bi+EM+SA-MoA-8 Utilizing the Chiral Induced Spin Selectivity Effect to Achieve Simple Spintronics Devices, Yossi Paltiel, The Hebrew University of Jerusalem, Israel

With the increasing demand for miniaturization, nano-structures are likely to become the primary components of future integrated circuits. Different approaches are being pursued towards achieving efficient electronics, among which are spin electronics devices (spintronics) [1]. In principle, the application of spintronics should result in reducing the power consumption of electronic devices.

A new, promising, effective approach for spintronics has emerged using spin selectivity in electron transport through chiral molecules, termed Chiral-Induced Spin Selectivity (CISS) [2]. Recently, by utilizing this effect we demonstrated a magnet-less magnetic memory [3,4]. Also we achieve local spin-based magnetization generated optically at ambient temperatures [5,6]. The locality is realized by selective adsorption of the organic molecules and the nano particles [7]. Lastly we have been able to show chiral proximity induced magnetization on the surface of ferromagnetic and superconducting materials. The magnetization is generated without driving current or optically exciting the system [8,9].

In the talk I will give a short introduction about spintronics and the CISS effect. Then I will present ways achieve simple spintronics devices utilizing the effect.


Tuesday Morning, October 31, 2017

2D Materials Focus Topic
Room 15 - Session 2D+AS+SA+SP-TuM

2D Materials Characterization including Microscopy and Spectroscopy
Moderator: Sara Barja, Materials Physics Center, San Sebastián, Spain

8:00am 2D+AS+SA+SP-TuM-1 Electronic Structure of Oxygen-Intercalated Graphene on Iridium Interface. Yi Lin, Y Li, Columbia University; J Sadowski, Brookhaven National Laboratory; J Dadap, W Jin, R Osgood, Columbia University; M Hybertsen, Brookhaven National Laboratory

We report experimental and theoretical work to understand how oxygen intercalation changes the image potential state and surface state electronic structure in a metal/graphene interface. We use tunable angle-resolved two-photon photoemission spectroscopy to probe the evolution of the electronic band structure of an epitaxially grown monolayer graphene on Ir(111) as it undergoes through a cycle involving oxygen intercalation and deintercalation. Oxygen intercalation is carried out in situ and LEED is used to determine the crystallinity of the interface in the presence or absence of the intercalated oxygen. The image state manifold and its effective mass are examined. The photoemission intensity variation in momentum space and the observation of an oxygen induced state are discussed. Furthermore, a recently proposed effective potential model at the graphene/metal interface is developed further by us to accommodate oxygen intercalation and interpret our experimental electronic structure variation with good agreements.

We acknowledge support from the US Dept. of Energy, Office of Basic Energy Sciences, under Contract Numbers DE-FG 02-04-ER-46157, DE-FG02-90ER14104, and DESC0002704.

8:20am 2D+AS+SA+SP-TuM-2 Graphene Moiré Pattern Ultra-High Resolution Atomic Force Microscopy, Gerald Pascual, B Kim, K Lee, Park Systems Inc.

The high-resolution resolution of AFM was demonstrated in a Graphene/hexagonal Boron Nitride (hBN) sample evaluation conducted by AFM. The sample consisted of hBN substrate overlaid with a Graphene layer and was scanned under ambient air. The purpose of the evaluation was to assess the AFM ability to characterize the topography of the moiré pattern that was created when one layer was set on top of the other and offset by rotation. Using non-contact AFM mode and a standard AFM probe tip, the AFM was able to successfully image the moiré pattern super lattice constant of the sample in scans as large as 500 x 500 nm. In the higher magnification image taken at a scan size of 60 x 60 nm provides the clear evidence that not only are the super lattice constants of the moiré pattern about 15 nm [1] in width, but that the spacing between each striation on the moiré pattern is roughly 4-5 nm in length. Observations of such striations in Graphene/hBN systems have been previously reported [2]. This latter distance is in line with the expected tip radius curvature values for the AFM tip used to acquire all four sets of data.


8:40am 2D+AS+SA+SP-TuM-3 Surface and Interface Properties of 2D MoS2 and WSe2 Materials, Chio-Seng Chang, Institute of Physics, Academia Sinica, Taiwan; Republic of China; Tiaoyi Taiwan; Y Lee, National Tsing-Hua University, Taiwan, Republic of China

INVITED

Two dimensional layered transition metal dichalcogenides (2D TMD), such as MX2 (M = Mo, W and X = S, Se), have offered exciting new physics and chemistry, as well as potential applications in energy harvesting, electronics, and optoelectronics. Surface and interface properties of these 2D materials are fundamental to further advance them on scientific exploration and device fabrication. In this talk, we will demonstrate the growth of various TMD monolayers using ambient-pressure chemical vapor deposition. The quality of a MoS2 monolayer was examined by scanning probe microscopy, electron microscopy, and optical spectroscopy. We will discuss the key issues associated with the surfaces and interfaces of these materials.

9:20am 2D+AS+SA+SP-TuM-5 Spectroscopic Investigation of Plasma-Fluorinated Monolayer Graphene and Application for Gas Sensing, Hui Zhang, Shanghai Institute of Microsystem And Information Technology, China; J Guo, Lawrence Berkeley National Laboratory; X Sun, Soochow University

A large-area monolayer fluorinated graphene (FG) is synthesized by a controllable SF6 plasma treatment. The functional groups of FG are elucidated by various spectroscopies, including Raman, X-ray photoemission spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS). Raman results suggest that the defects are introduced into the monolayer graphene during the fluorination process. The fluorine content can be varied by the plasma treatment and can reach the maximum (~24.6 at% F) under 20 s plasma treatment as examined by XPS measurement. The angle dependent NEXAFS reveals that the fluorine atoms interact with the graphene matrix to form the covalent C-F bonds, which are perpendicular to the basal plane of FG. FG is applied as gas sensing material and owns much better performance for ammonia detection compared to the pristine graphene. Based on our DFT simulation results, the fast response/recovery behavior and high sensitivity of the FG gas sensor are attributed to enhanced physical absorption due to the C-F covalent bonds on the surface of FG.

9:40am 2D+AS+SA+SP-TuM-6 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of 2D Crystals on Silicon Oxide, Taisuke Ohta, M Berg, Sandia National Laboratories, Center for Integrated Nanotechnologies; C Chan, Sandia National Laboratories; K Keyshar, Rice University; G Gupta, University of Louisville; P Ajoyan, Rice University; A Mohite, Los Alamos National Laboratory

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals would line up with respect to each other. Defined as an energy separation between the vacuum level and the highest occupied electronic states, the ionization energy is of particular importance for atomically-thin two-dimensional (2D) crystals to predict the performance of their heterostructures useful in high performance electronics and opto-electronics. Ionization energies have been investigated based on theoretical calculations, but to the best of our knowledge, no systematic experimental confirmation is reported for the wide range of 2D crystals despite their importance.

Here, we present a new approach to study the electronic properties of prototypical 2D crystals, graphene, MoS2, WS2, and MoSe2 monolayer and multilayer flakes, supported on thick silicon oxide (SiO2) film using a photoemission electron microscopy combined with a deep ultraviolet (DUV) illumination. We determine the band alignments of monolayer to multilayer junctions in these four materials, and show that the ionization energy decreases from MoS2, WS2, to MoSe2, as predicted by density functional calculations. We also present in situ data that show the charging of the 2D crystals thanks to the relatively low total photoemission current due to the low energy excitation by the DUV light. This study reveals a new metrology to uncover electronic properties intrinsic to 2D crystals supported on SiO2 substrates that interact minimally with the overlying 2D crystals.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). T. O. is supported by the CINT user program and Sandia LDRD. The work performed by M. B. and C. C. are supported by a U.S. DOE, Office of Energy Efficiency and Renewable Energy SunShot Initiative award for BRIDGE (DE-FOA-0000654 CP525859). K. K. was supported by the Army Research Office MURI grant W911NF-11-1-0362. A. D. M. is supported by LANL LDRD program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

11:00am 2D+AS+SA+SP-TuM-10 STM and STS Study of MoS2/WS2 Heterostructures Grown by Chemical Vapor Deposition, Fan Zhang, Virginia Polytechnic Institute and State University; Z Lu, Tsinghua University; H Cheng, K Park, Virginia Polytechnic Institute and State University; L Jiao, Tsinghua University, PR China; C Tao, Virginia Polytechnic Institute and State University

2D materials like atomically thin transition metal dichalcogenides (TMDs) have received tremendous attentions for their unique properties and high potential applications. Recent developments on synthesis of 2D heterostructures through the chemical vapor deposition (CVD) method...
provide an unprecedented opportunity to create and tune the intriguing electronic and optical properties of 2D materials such as engineering the band gaps. These 2D heterostructures have a wide range of applications in electronics and optics, for example, tunneling transistors, single-photon emission devices and photovoltaic devices. To further optimize and design 2D heterostructures, it is essential to investigate the structural and electronic properties at the atomic scale, which is however still lacking.

In this presentation, we will focus on a high-quality MoS$_2$/WS$_2$ heterostructure grown on SiO$_2$ using the CVD method. Scanning tunneling microscopy (STM) and spectroscopy (STS) were performed to study the morphology and band structures of both MoS$_2$ monolayer and MoS$_2$/WS$_2$ heterobilayer. Atomically resolved STM images were obtained on the monolayer, heterobilayer and the interface between the monolayer and heterobilayer. The height histograms acquired respectively on the monolayer and the heterobilayer indicate that the heterobilayer is higher than the monolayer with a height difference of $0.85 \pm 0.10$ nm. The roughness of the monolayer and heterobilayer was for the first time quantified by STM. The root mean square (RMS) roughness of the heterobilayer is $0.253 \pm 0.020$ nm compared with $0.362 \pm 0.031$ nm of the monolayer. We also performed STS measurements on the system. Our STS results and density functional theory (DFT) calculations reveal the band gaps of the heterobilayer and the MoS$_2$ monolayer, which are similar to the previously reported results on MoS$_2$/WS$_2$ heterostructures fabricated through the mechanical exfoliation method.

11:20am 2D+AS+SA-TuM-11 Determine the Band Alignment of 2D Semiconductor Heterostructures by Photoelectron Spectromicroscopy. L Chang, National Synchrotron Radiation Research Center, Taiwan, Republic of China; Y Wang, Y Ku, National Tsing Hua University, Republic of China; Y Kuo, H Shiu, Chia-Hao Chen, National Synchrotron Radiation Research Center, Taiwan, Republic of China

Semiconductor heterojunction (HJ) band alignment is the most important factor for the functioning of the Hi-based devices. Therefore, the prediction and determination of the HJ band offset is always a scientifically interesting and technologically important topic. As the 2D materials emerged as the building blocks for the devices with molecular thickness, the determination of band alignment of the van der Waals HJs is becoming a critical issue.

Due to the nature of the molecular thickness and the lack of large area 2D crystal, a microscope with surface sensitivity is an ideal tool to study the fundamental properties of the 2D heterostructures.

In this regard, we have employed a synchrotron radiation based scanning photoelectron spectromicroscopy (SPESM) to study the chemical and electronic structures of the van der Waals HJs, include the single-layer transition metal dichalcogenides, and graphene/GaN HJs. In this presentation, I will report some of the band alignments of these 2D semiconductor heterostructures.

Actinides and Rare Earths Focus Topic Room 22 - Session AC+AS+SA-TuM

Nuclear Power, Forensics, and Other Applications Moderator: James G. Tobin, University of Wisconsin-Oshkosh

8:00am AC+AS+SA-TuM-1 Design of Synergistic Protein-ligand Systems for f-Element Coordination, where Separation, Decontamination and Nuclear Medicine Meet, Rebecca Abergel, Lawrence Berkeley National Laboratory

INVIITED Separation of elements from the 4f- and 5f- series is a challenging task due to the similarities in their ionic radii and the existence of most of these metal ions in the trivalent oxidation state. Understanding the fundamental bonding interactions between those metal centers and selective ligands presents a rich set of scientific challenges and is critical to the development of new separation strategies as well as to a number of applied problems such as the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques to investigate specific lanthanide and actinide coordination features by bio-inspired catecholamide and hydroxypridinone hard oxygen-donor ligands. Using such ligands allows the solution differentiation of different metals through stabilization in specific oxidation states and provides information on their respective electronic structures. In addition, X-ray diffraction analyses using the mammalian iron transport protein siderozalin as a crystallization matrix revealed remarkable aspects of the protein’s interactions with chelated metals, establishing series of isostructural systems that can be used to derive trends in the later 5f-element sequence, when combined with theoretical predictions. These results will be discussed with a perspective on how such studies have important implications for the use of spectroscopic and thermodynamic methods to exploit the fundamental knowledge of the role of f-electrons in actinide bonding for the development of new transport, separation, luminescence, and therapeutic applications.

8:40am AC+AS+SA-TuM-3 Image Processing And Particle Analysis Of Fission-Truck-Analysis In Nuclear Forensic, Itzhak Halevy, Department of Physics, NRCN, Israel; U Admon, (Retiree), IAECS-NRCN, Department of Materials, Beer-Sheva Israel, Israel; E Chinea-Cano, Office of Safeguards Analytical Services (SGAS), International Atomic Energy Agency (IAEA), Austria; A Weiss, Faculty of Engineering, Bar-Ilan University, Israel; N Dzigal, Office of Safeguards Analytical Services (SGAS), Austria; E Bobill, Department of Physics, IAECS-NRCN, Israel

Particle analysis is a key discipline in safeguards and nuclear forensic investigations, as well as in environmental research. The radioactive Particles are usually in the micrometric size range, and intermixed within huge populations of other particles, like air-borne dust, soil, industrial exhaust pollutants or estuary sediments.

We are using the Fission Truck Analysis (FTA) technique. In that technique plastic detectors used for raping a Lexan catcher with the particles and together are radiated in nuclear reactor with thermal neutrons. The Fission Truck are trucks done by the fission products. The fission material is dominant in producing the trucks, namely the $^{235}$U isotope. The Fission Truck could be more visible by special etching and can be used to locate the particles.

From that point, the analysis of Fission Truck is an image processing. Scanning the detectors is a time-consuming procedure. Automated scanning and fission star recognition will make all the Analysis easier to quantify.

The challenge, therefore, consists in scanning and imaging a relatively large area detector, at a resolution of about $1\mu$m, and locating the FT clusters while rejecting the artefacts.

Image processing was done using the Fiji distribution of ImageJ. The algorithms shown in this report were implemented using either the ImageJ macro language or the ImageJ Python scripting engine. Basic noise removal, illumination correction and Segmentation are the basic of the imaging analysis.

I case of large area detector a set of picture will be taken and by stiching a large picture will be composed.

Roundness and endpoint thresholds can be adjusted to obtain fewer false negatives at the expense of more false positives. A receiver operation characteristic (ROC) can be used to characterise this.

The high and low threshold determination in the hysteresis thresholding step should be improved.

After the automated procedure the operator can go over the FT and decide if to add stars that were not found by the software or to cancel stars that are artifact.

Correlation between forensic and image processing parameters will be defined. Even that stars are coming from $^{235}$U only and it is no one to one connected only to enrichment we still think that the shape, color, number of end points and roundness can be parameters to indicates different forensic properties.

9:00am AC+AS+SA-TuM-4 Application of Linear Least Squares to the Analysis of AES Depth Profiles of Plutonium Oxides, Scott Donald, A Nelson, Lawrence Livermore National Laboratory

Application of the linear least squares (LLS) methodology allows for quantitative determination of variation in material composition with depth, as well as permitting an understanding of differences resulting from changes in the method of preparation. LLS fits were applied to decompose and enhance the interpretation of spectra obtained by Auger electron spectroscopy (AES) during depth profiles of oxidized plutonium surfaces. By means of the LLS algorithm, chemical state assignments of the $^{239}$Pu, $^{240}$Pu, $^{241}$Am+ $^{241}$Cm, $^{242}$Cm, and $^{244}$Cm Auger transitions were determined and the existence of a subsurface oxy-carbide layer was identified, with confirmation provided from comparison to previous measurements of standard samples.
The work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:20am AC+AS+SA-Tum-5 Physical and Chemical Characterization of Solid Pu and Np Sources after Multi-year Exposure to Environmental Conditions, Brian Powell, Clemson University

An in situ field scale radionuclide vadose zone transport experiment at the United States Department of Energy Savannah River Site is being operated by Savannah River National Laboratory and Clemson University scientists. In this experiment, plutonium and neptunium solid sources are buried in 61 cm long x 10 cm diameter lysimeters which are open to precipitation. Such experiments provide the opportunity to observe changes in the microcrystalline structure of plutonium and neptunium solid phases under various environmental conditions. In the current experiments, sources of neptunium and plutonium in multiple initial oxidation states and chemical forms have been deployed for 2-5 years of field exposure. These sources include Pu(VI)2HCO3(s), Pu(VI)4CO3(s), Pu(III)3CO3(s), Pu(V)2O(s), Np(V)2O(s) and NpO2NO3(s). X-ray absorption spectroscopy (XAS) analysis of initially Pu(V)HCO3(s) sources archived in an inert atmosphere and sources exposed to lysimeters indicate some reduction to Pu(IV) within the sources leading to the formation of Pu(IV)O(s). Thus, there appears to be an auto-reduction of NH4Pu(V)O4(s) to Pu(IV)O(s) even under inert conditions. However, solvent extraction on archived field-deployed sources show the archived source still contains around 40% Pu(IV) whereas the same source from a field lysimeter deployed for 2.5 years contained less than 10% of Pu(IV). XAS and electron microscopy studies have demonstrated differences between Pu(V)O(s) formed via reduction of Pu(V)O2HCO3 and initially Pu(IV)O2(s) formed from precipitation of a Pu(IV) solution. The behavior of initially Np(V)O(s) sources was quite different showing oxidation to Np(V) and subsequent downward transport of more soluble Np(V)O4(s). The oxidation of Np(IV)O(s) leads to a formation of a much more disordered solid phase with a significantly altered morphology than the initial Np(V)O(s). The results of these experiments will be discussed in terms of evaluating the history of the sample through analysis of the microcrystalline structure and the influences of aging under various environments.

11:00am AC+AS+SA-Tum-10 Synchrotron Radiation Investigation of F-element Extraction from a Carboxylic Acid Functionalized Porous Aromatic Framework, David Shuh, Lawrence Berkeley National Laboratory; S Demir, N Brune, University of California Berkeley, LBNL; J Van Humbeck, J Mason, University of California Berkeley; T Plakhova, Lomonosov Moscow State University, Russia; S Wang, University of California Berkeley, LBNL; G Tian, S Minasian, T Tyliszczak, Lawrence Berkeley National Laboratory; T Yaita, T Kobayashi, Japan Atomic Energy Agency; S Kalmykov, Lomonosov Moscow State University, Russia; H Shiwaku, Japan Atomic Energy Agency; J Long, University of California Berkeley

Porous aromatic frameworks (PAFs) incorporating a high concentration of acid functional groups possess characteristics that are promising for use in separating lanthanide and actinide metal ions, as required in the treatment of radioactive waste. These materials are shown to be indefinitely storable to concentrated acids and bases, potentially allowing for multiple adsorption/stripping cycles. Additionally, the PAFs combine exceptional features from metal organic frameworks (MOFs) and inorganic activated carbons giving rise to tunable porous surfaces and maximum chemical stability. The adsorption of selected metal ions, Sr2+, Fe3+, Nd3+, and Am3+, from aqueous solutions employing a carboxyl-based PAF, BP-7 (Berkeley Porous Organic Framework) has been investigated. This material displays high metal loading capacities together with excellent adsorption selectivity for neodymium over strontium. X-ray absorption spectroscopy studies show that the stronger adsorption of neodymium is attributed to multiple metal ion and binding site interactions resulting from the densely functionalized and highly interpenetrated structure of BP-7. Recyclability and combustibility experiments demonstrate that multiple adsorption/stripping cycles can be completed with minimal degradation of the polymer adsorption capacity.

11:20am AC+AS+SA-Tum-11 The Effect of Al2O3 Encapsulation Using Atomic Layer Deposition on the Photoluminescence, Water and Thermostability Properties of SrAl2O4: Based Phosphors, Enklu Karaacagolu, E Ozturk, Karamanoglu Mehmetbey University, Turkey; M Uyaner, Selcuk University, Turkey

Aluminate based phosphors (MAI2O4, MAI2Al2O7, M= Sr, Ba, Ca, etc.) are chemically unstable against water and even moisture. Moreover, some of phosphors, like green emitting phosphorescent materials’ luminescence properties, but not their structural properties, are affected negatively during reheating applications because the 2+ ionic state of europium is oxidized to 3+ in open atmosphere low temperature heating process thus limiting their applications. Their hydrolysis process were studied and analyzed intensively by researchers. Changes of pH value of suspensions, the structures and optical properties of the hydrolysis of phosphor structures had been investigated. In this research, to prevent or minimize this degradation, to enhance the water resistance and to maintain the phosphorescence properties, an Al2O3 coating on the surface of SrAl2O4 based phosphor pellets (1 mm thickness) were prepared using Atomic Layer Deposition (ALD) method with Trimethylaluminum (TMA) precursor. The investigation of phase formation of strontium aluminate was analyzed by thermal analysis (DTA/TG) until 1500 °C. The SrAl2O4 with Monoclinic structure in single phase having lattice parameters a=8.44365 Å, b=8.82245 Å, c=5.15964 Å and α=90° β=90° γ=90° were obtained according to XRD analysis. The photoluminescence (PL) results of both open and reduced atmosphere synthesized phosphors with excitation and emission wavelengths and decay time were determined by a PL spectrometer at room temperature. The reduced and open atmosphere synthesized samples have different photoluminescent characteristics because of ionic state of europium in 2+ and 3+ at reduced atmosphere and open atmosphere, respectively. Moreover, it was obtained that the main crystal, SrAl2O4, had photoluminescent properties. The surface analysis of phosphors as morphology and elemental analysis (SEM/EDX), X-ray diffraction (XRD), water and heat resistance (thermostability), photoluminescence (PL) of the phosphors before and after encapsulation were discussed in detail.

Magnetic Interfaces and Nanostructures Division Room 11 - Session MI+2D+AC+SA+SS-Tum Novel Magnetic Order at Interfaces

Moderators: Axel Enders, University of Nebraska-Lincoln, Valeria Lauter, Oak Ridge National Laboratory

8:20am MI+2D+AC+SA+SS-Tum-2 Transition from Spatial to Magnetic Confinement in Graphene Quantum Dots, Fereshte Ghahre, D Walkup, C Gutierrez, NIST; Maryland NanoCenter UMD; J Rodriguez-Nieu, Harvard University; K Watanabe, T Taniguchi, National Institute for Materials Science, Japan; L Levitov, MIT; N Zhitenev, J Strosco, NIST

Recent progress in creating and probing graphene quantum dots has offered a new platform to investigate Klein tunneling related phenomena. The quasi-bound resonances in these circular resonators can be confined even further by the application of a perpendicular magnetic field where they condense into highly degenerate Landau levels. Here, we use scanning tunneling spectroscopy to visualize the transition from spatial to magnetic confinement in quantum dots created in graphene/boron nitride heterostructures. In high magnetic fields, electrons redistribute themselves due to coulomb interactions leading to compressible regions separated by incompressible strips.

8:40am MI+2D+AC+SA+SS-Tum-3 Chiral and Proximity Induced Magnetsim in Magnetic Multilayers and 2D Heterostructures, Hyunsoo Yang, National University of Singapore, Singapore

Invited

Topologically non-trivial chiral spin textures are present in systems with a strong Dzyaloshinskii-Moriya interaction (DMI) with a spatial extent of only tens to a few hundred nanometers. Thin film heavy metal/ferromagnetic bi- and multilayers have emerged as an ideal candidate for the demonstration of such devices due to their tunability through a variation of the constituent components and relative layer thicknesses. However, to date, no chiral spin textures have been observed in thick ferromagnetic multilayers in which the disparate magnetic layers are exchange coupled. Furthermore, previous observations required either the presence of an out-of-plane bias field or careful tuning of a geometric confining potential to stabilize the skyrmion structure. In this work, we have imaged the formation of room temperature Néel skyrmions in a symmetric Co/Pd multilayer with Lorentz transmission electron microscopy for the first time [1]. Importantly, the size of the observed skyrmions is significantly smaller than previously reported systems in which non-multilayer films are used. The formation and resolution of the internal spin structure of room temperature skyrmions without a stabilizing out-of-plane field in thick magnetic multilayers opens up a new set of tools and materials to study the physics and device applications associated with magnetic chiral ordering.
Due to the unique topology associated with their band structure, two-dimensional (2D) transition metal dichalcogenides (TMDs) such as WS$_2$, MoS$_2$, and WTe$_2$ provide a unique platform to develop novel electronics using the spin-valley degree of freedom. The incorporation of the heavy metal in the TMD suggests strong intrinsic spin orbit interactions, and could further result in a chiral DMI. However, confirmation of the DMI in such films and its effects on the spin ordering in the overlaying magnetic layer is lacking. Further, it has recently been predicted that orbital hybridization at the TMD/FM interface may occur and result in generation of a non-negligible magnetic moment in the TMD layer. In the present study we explore the interface induced magnetism in TMD/FM films. Finally, we also explore the effects of DMI and generation of chiral spin textures that result from it by measuring the imbalance between left and right-handed domains within the ferromagnetic layer. As the polarized neutron scattering is strongly dependent on spin chirality, this method has been utilized to study chiral magnetism in multilayer structures with strong DMI.


9:20am MI+2D+AC+SA+SS+TuM-5 Surface Magnetism Induced by Interstitial Defects in PbO, Elvis Arguelles, Osaka University, Japan; S Amino, A.L.M.T. Corp, Japan; H Nakashita, S Aspera, H Kasai, National Institute of Technology, Akashi College, Japan; W Dino, Osaka University, Japan

We investigated the possibility of employing the polycrystalline aPbO as a spintronics device by first principles calculations based on the density functional theory (DFT). In particular, we explored the effects of 3d transition metal atoms on the structural and electronic properties of the layered aPbO [001] surface. Since it has been proven that ferromagnetic signals in experiments are often detected in thin films[1] we used a 2x2, 3-layered surface slab model of aPbO with 20 Å of vacuum space to simulate this environment in this study. The impurity atoms are placed in between the surface and subsurface of the crystal. The results show that the interstitial Fe interstitial forms shorter bonds with the oxygen atoms located at the surface and second layers. Also, this impurity is found to induce magnetism in the host crystal with magnetic moment value of 2.25 µB, which is highly localised on the transition metal.

In the bonding process, the Fe’s lower energy lying d states form overlaps with nearest neighbour oxygen atoms with non-bonding d states situated near or at the Fermi level and are spin split. These spin split orbitals induce spin polarisation of p impurity states of oxygen atoms in the subsurface. Moreover, the magnetic order is determined using the energy difference between the antiferromagnetic and ferromagnetic states. The energy difference is 0.068 eV, suggesting that Fe interstitial impurities induce ferromagnetism in aPbO [2]. In this workshop, the effects of charge carriers to the magnetic properties will be briefly discussed. Finally, the position of the Fermi level in the density of states (DOS) suggests that in the case of α-PbO with Fe interstitials where the minority non-bonding d states are partially filled, the Zener’s ferromagnetic double exchange mechanism may be dominant and stabilising the ferromagnetic state.

References:

9:40am MI+2D+AC+SA+SS+TuM-6 XMCD Quest for Magnetic Proximity Effect in Ferromagnetic Insulator/Non-Magnetic Metal Interfaces, Andrei Rogolev, F Wilhelm, European Synchrotron Radiation Facility, France

The rise of spin current physics together with enormous technological advances to engineer layered structures with tailored spin-orbit interactions have placed 4d and 5d transition metals at the heart of the emerging fields of spinorbitronics, magnonics and caloritronics. In this context, magnetic properties at the interfaces between a ferromagnetic materials and non-magnetic metals with large spin-orbit coupling play a central role. Some of those heavy metals like Pt or Pd are known to exhibit so-called magnetic proximity effect, i.e. they acquire interfacial induced magnetic moments whenever they are in contact with 3d metallic ferromagnets. However, when they are grown on magnetic insulators, e.g. yttrium iron garnet (YIG), whether induced magnetic moments are indeed ubiquitous is still an open question as contradictory reports have been published. This is indeed the key question for correct interpretation of the spin Hall magnetoresistance or the newly discovered unidirectional magnetoresistance phenomena and, in more general, to understand mechanisms of pure spin currents generation. To answer this question and to unravel a possible role of magnetic proximity effects at ferromagnetic/non-magnetic interfaces, X-ray magnetic circular dichroism (XMCD) spectroscopy appears to be the method of choice due to its element selectivity and high sensitivity. In this talk, we present a thorough review of XMCD experiments aimed at detection of magnetic proximity effect in a variety of ferromagnetic insulator/non-magnetic metal interfaces.

11:40am MI+2D+AC+SA+SS+TuM-12 Depth-Dependent Measurement of Atomic Valence and Magnetization in La$_2$Sr$_2$MnO$_6$: Magnetic Thin Films, Mikel Holcomb, R Trappen, S Kuman, N Mottaghi, S Yousef Sarraf, C Huang, C Cabrera, West Virginia University

Magnetic thin films often lose their magnetic order and even bulk materials can have significant deviations of the magnetic order and other properties near surfaces and interfaces. In strongly correlated oxides, there are many competing parameters affecting the material properties, complicating the understanding of these systems. We utilize a combined approach of bulk and surface sensitive techniques measuring many film thicknesses to back out layer-by-layer properties in La$_2$Sr$_2$MnO$_6$ (LSMO) thin films. Small changes from the bulk are observed for surfaces and interfaces. We will compare these models with theoretical predictions. LSMO has been widely proposed for diverse applications such as tunnel junctions and solid oxide fuel cells. Experimental support is provided by NSF (DMR-1608656). Theoretical support is provided by DoE (DE-SC0016176).

12:00pm MI+2D+AC+SA+SS+TuM-13 Coherent Magnetization Rotation of FeGa/NiFe Multilayers via Strain-Inducing Electric Field, Colin Rementer, University of California at Los Angeles; M Jamer, NIST; A Barra, University of California at Los Angeles; J Borcher, A Grutter, B Kirby, NIST; G Carman, J Chang, University of California at Los Angeles

The ability to reduce the size of antennae would enable a revolution in wearable electronics, extendable to implantable electronic devices. Antenna miniaturization could be enabled by multiferroic materials, which enable the efficient control of magnetic via electricity. Multiferroic antennae, composed of coupled ferromagnetic and piezoelectric phases, could reduce antenna size by up to five orders of magnitude. This requires a magnetic material that is low loss, has an easily rotatable magnetization and is able to convert magnetic field to strain via magnetostriction.

Galfenol (Fe$_2$Ga$_5$, or FeGa) is a promising magnetic material due to its large magnetostriction (>200 ppm), high piezomagnetic coefficient (3 ppm/Oe), and high stiffness (70 GPa), but has high loss in the GHz regime. Permalloy (Ni$_81$Fe$_19$ or NiFe) is a soft magnetic material that has very low loss in the GHz regime (<20 Oe) but almost no magnetostriction. In this work, multilayer laminates containing alternating FeGa/NiFe layers were fabricated to reduce loss at high frequencies and properties were tuned via layer number and thickness. In this work, optimized multilayer laminates containing alternating FeGa/NiFe layers were shown to exhibit desirable magnetic softness (<20 Oe), narrow FMR line width (<40 Oe), high permeability (>400), and strong magnetostriction (>70 microstrain). The focus of this work is to determine if the rotation of the magnetization of the individual layers is coherent with applied strain.

Polarized neutron reflectometry was used to determine the depth profiles of the structure and in-plane vector magnetization as functions of applied magnetic field and voltage. Initial studies showed that a FeGa/NiFe superlattice with the structure (20 nm FeGa/7 nm NiFe)/20 nm FeGa demonstrated coherent and linear rotation of magnetization with applied strain. To probe the thickness dependence of this rotation, three single NiFe/FeGa bilayers were fabricated on PMN-PT [011] with 40 nm, 20 nm and 7 nm of NiFe on a base layer of 20 nm FeGa. Application of 400 V results in an enormous increase in spin-flip scattering, unambiguously demonstrating a substantial rotation of the magnetization perpendicular to the applied magnetic field direction for all samples measured. Micromagnetic and finite element simulations support the experimental results, showing coherent rotation of the magnetization with only small deviations with thicker NiFe layers. These measurements provide direct evidence of a voltage-induced rotation of the both the NiFe and FeGa magnetization as well as a means to separate the response of the magnetostrictive and non-magnetostrictive layer components.
Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 9 - Session SA+MI-TuM

Overcoming the Temporal and Spatial Limits of X-Ray Scattering Methods for In-Situ Analysis
Moderators: Olivier Renault, CEA-University Grenoble Alps, France, Zahid Hussain, ALS-LBNL, Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy

8:20am SA+MI-TuM-2 SA Highlight Talk: Diffraction Limited Storage Rings and Free Electron Lasers --- Why do we need both? Wolfgang Eberhardt, DESY-CFEL, Germany

Accelerator driven photon sources have experienced a phenomenal development and success over the last decades. Worldwide many thousands of scientists travel to these facilities to conduct their research and new and upgraded facilities are under construction in several countries around the world. While storage ring based facilities have been at the heart of this effort until recently, the attention has somewhat turned to the construction of free electron laser facilities. As the peta-cycles for each of these facilities is in the range of 100s of million $, and even surpassing 1 B$, the question arises, whether science and society really needs both kind of facilities.

In this talk I will give examples of experiments that are unique to each of these light sources, emphasizing the need for both --- state of the art DLSR’s and FEL’s --- to meet the challenges of future science and society.

8:40am SA+MI-TuM-3 Understanding Solar Cells Structure and Functioning via GISAXS and GIWAXS, Peter Müller-Buschbaum, Technische Universität München, Germany

INVITED

Next generation solar cells are an interesting alternative to conventional silicon based solar cells as the feature new possibilities introduced by using a different class of materials namely polymers. The production of next generation solar cells has the potential to become very cheap and easy. Moreover, the use of polymers allows for flexible solar cells and lightweight devices, which will be usable in a very different fashion as compared to the immobile silicon solar panels. In addition, the energy payback times of next generation solar cells are significantly shorter as compared to the today’s silicon solar cells. However, despite all these significant advantages of next generation solar cells, still fundamental knowledge is very limited.

In particular, it is challenging to detect the complex morphology, which are necessary to have high efficiency organic solar cells. The combination of grazing incidence small and wide angle x-ray scattering (GISAXS and GIWAXS) allows for overcoming these challenges.1,2 The crystalline structure is probed with GIWAXS and the mesoscale structure is determined with GISAXS. Based on selected examples, the impact of different layers in the functional stack build-up of organic solar cells,3-6 in-situ studies during printing7 and in-operando studies of organic solar cells8 are presented.

References

Tuesday Morning, October 31, 2017
gradual shift in the photoemission onset up to the Fermi energy indicates a
change in the character of the gold clusters from non-metallic to metallic.
The results are compared with theoretical work and previous investigations
to validate the XUV-PES method. Static photoemission is then further
utilized to monitor the electronic structure of Zn clusters on p-Si(100) as a
function of Zn deposition. The transition from non-metallic to metallic Zn
character is observed at 0.16 ML of Zn coverage. Furthermore, the
femtosecond pump-probe XUV-PES technique is employed to induce a
charge transfer from the p-Si(100) substrate to the Zn clusters and to
measure in real time the charge trapping at the Zn clusters as well as the
subsequent charge relaxation. The ultrafast charge carrier dynamics
investigations are performed as the Zn dimensionality is increased from
small clusters composed of a very few atoms to large collections of atoms
to extended Zn films.

12:00pm SA+MI-TuM-13 Direct Observation of TiO$_2$ Exciton
Recombination, Geoff Thornton, University College London, UK; Y Zhang, D
Payne, C Pang, University College London, UK; C Cacho, R Chapman, E
Springate, STFC Rutherford Appleton Laboratory, UK
Exciton recombination pathways are of paramount importance in
photocatalysis because they determine the lifetime of the chemically active
electrons and holes, and hence the catalytic efficiency. These pathways are
not known in detail even for a prototypical material such as TiO$_2$, where the
related process of electron trapping is important in a broader range of
applications (eg resistant switching). Here we use time-resolved
femtosecond pump-probe photoemission spectroscopy (TRPES) to
investigate exciton recombination and electron trapping in a state resolved
fashion. This employed an XUV probe following an infra-red or UV pump.
When an infra-red pump is employed, electrons in polaronic band gap
states (BGS) are excited to the bottom of the conduction band. The
subsequent recapture time of 50±10 fs is determined by directly
monitoring the intensity change of the BGS and hot electrons in TRPES
spectra. When a UV pump is employed, electrons are excited either from
the BGS to a resonance in the CB, or from the top of the valence band (VB)
to the bottom of the CB. The same trapping of hot electrons is observed as
for infra-red excitation. In addition, a long lifetime component (>1 ps) of
the hot electron decay and the BGS recovery are observed, pointing to trap
assisted exciton recombination.
2:20pm AC+MI+SA+SU-TuA-1 Magnetic Susceptibility, Magnetic Resonance, and Bonding in Actinide Complexes: Ab-initio Calculations, Jochen Autschbach, University of Buffalo, SUNY

Actinide complexes exhibit fascinating magnetic properties and interesting chemical bonding. An on-going research project in our group is devoted to first-principles calculations of magnetic resonance parameters (NMR, EPR), magnetic susceptibilities, and other spectroscopic parameters of actinide complexes in relation to their chemical bonding, in particular regarding the involvement of the 5f shell in metal-ligand bonding. We will present results from recent computational studies of magnetic resonance parameters and the magnetic susceptibility of f-element complexes utilizing relativistic quantum chemical methods.


3:00pm AC+MI+SA+SU-TuA-3 Combining DMRG with Standard Relativistic Multireference Methods to Probe the Properties of Strongly Correlated Systems: Plutonium Oxides, Valérie Vallet, S Kervazo, CNRS / University of Lille, France; F Réal, University of Lille, France; A Severo Pereira Gomes, CNRS / University of Lille, France; F Virot, IRSN, France \textbf{INVITED}

Actinide-containing complexes present formidable challenges for electronic structure methods due to the large number of degenerate or quasi-degenerate electronic states arising from partially occupied 5f and 6d shells. In particular, we focus our study here on volatile forms of plutonium such as PuO2, PuO3 or PuO2(OH)2, for which spectroscopic and thermodynamics properties are of interest.

To attain an accuracy comparable to that of experiments, highly accurate calculations including static and dynamic correlation effects as well as relativistic effects are required. Conventional multi-reference methods, however, can treat active spaces that are often at the upper limit of what is required for a proper treatment of species with complex electronic structures and large number of valence orbitals involved in chemical bonds, leaving no room for verifying their suitability.

In this work, we address first the issue of properly defining the active spaces in such calculations, and introduce a protocol to determine optimal active spaces based on the use of the Density Matrix Renormalization Group algorithm and concepts of quantum information theory.

The guidance offered by this protocol allows us to define the suitable active space to compute the electronic structures and the nature of the ground states with the desired accuracy, i.e. the clear multi-reference character of the wave-function of those compounds requires that the energies of formation to be computed with multi-configurational quantum chemical methods like CASSCF and CASPT2 and with spin-orbit interaction, treated here \textit{a posteriori} with the state-interaction RASSI method. Specifically, our results illustrate the complex multi-configurational character of PuO2. The computed thermodynamics quantities reach a high accuracy allowing us to predict the composition of the released volatile products.
approach demonstrates the power of joint theoretical and experimental efforts in creating bioactive materials with specifically and independently controllable characteristics (7).

References

3:00pm Bi+AS+MI+SA-TuA-3 Plant Virus Particles for 2D and 3D Architectures on Surfaces, V Rink, University of Kaiserslautern, Germany; M Braun, RLP Agroscope GmbH, Germany; M Ani, University of Kaiserslautern, Germany; K Boonrood, RLP Agroscience GmbH, Germany; C Müller-Renno, RLP Agroscience GmbH, Germany; G Krcaæ-Gehring, RLP Agroscience GmbH, Germany; Christiane Ziegler, University of Kaiserslautern, Germany

Biohybrid materials consist of biological entities and artificial, often inorganic materials. These biohybrids may be used in many fields of applications, ranging from biosensor to implant materials. In this context, bottom-up approaches, in which small elementary building blocks of matter are used to form larger elements through self-assembly have gained a lot of interest.

Plant viruses are promising candidates for such building blocks. Because of their simple structure and pre-defined size and form they have a high potential for self-assembly. Furthermore they can be genetically manipulated to create new functionalities by extending the capsid with different side chains.

We could show that unspecific electrostatic interactions govern the formation of large ordered 2D structures of self-assembled icosahedral tomato bushy stunt virus (TBSV) particles. By adding amino acid side chains to the capsid subunit the isoelectric point of the virus is changed. Thus by the right combination of virus modification, substrate and pH (and as a minor effect ionic strength) one can control the dimensions of 2D virus islands which may form layers with macroscopic dimensions. Specific structures in these 2D layers may be introduced by substrates which are pre-structured, e.g. by nano imprint lithography.

In addition to the electrostatic control the amino acid side chains allow also more specific interactions. Examples are histidine side chains interacting with Ni ions or gold binding peptide side chains with Au. With these specific interactions, also the third dimension is accessible. This opens the possibility to play with viruses in a kind of nano Lego which will soon become reality.

In this contribution we will show a scanning force and scanning electron microscopy study of the self-assembly of 2D and 3D structures of TBSV on Si and mica surfaces. The three dimensional structure is based on a homogeneous layer consisting of virus-particles carrying additional 4xAsp6xHis side chains (lowest stack). For the following second stack the chemical selectivity of these side chains to Ni ions (here: Ni-nitrilotriacetic acid (Ni-NTA) carrying a 5 nm Au nanoparticle was utilized. Au-binding virus-particles interact with these Au particles and create the third stack of this 3D virus architecture. The success of this strategy could be proven by SFM height measurements which reveal a height in the range of 66 nm, which corresponds to two layers of virus particles (30 nm each) coupled by Ni-NTA.


Tuesday Afternoon, October 31, 2017
some critical limitations for these analyses. As the high-performance SIMS instruments require high vacuum, a careful consideration of sample preparations is often needed. For example, advanced methods are necessary to prepare and measure complex hydrated bacterial biofilm structures. Also, in the pharmacological imaging of potential drug candidates at their targets, the positioning of water soluble drug compounds within cells or tissues can be altered by pre-treatment processes such as drying, resin-embedding or histological fixation. Advanced cryo-preparation methods are necessary for immobilisation of water in these samples to prevent the ultrastructural reorganisation and the loss or translocation of water-soluble molecules, to circumvent the use of chemical fixation and to enable their analysis in high-vacuum of mass spectrometry instruments.

The UK’s National Centre of Excellence in Mass Spectrometry Imaging [NICE MSI] at NPL has a special focus on the development of advanced solutions to challenging measurements. Our recently innovated 3D OrbiSIMS instrument has the capability to handle and measure cryogenically-prepared samples. The instrument is equipped with a vacuum cryo transfer system that is compatible with cryo-SEM and cryo-TEM. A shuttle chamber allows the interchange of samples, in vacuum and cryogenically, between cryo-preparative equipment and the 3D OrbiSIMS instrument. This presentation will show our recent developments of the cryo-SIMS methodologies. Different sample cryo-preparation techniques will be compared, such as the analysis performed on frozen-hydrated vs. frozen-dehydrated mammalian cells. The application of cryo-SIMS to a range of biological samples including cells, bacteria, biofilms and organic reference samples will be presented. Focus will be given to the use of different types of cryo-protectants, often required for the vitrification of thicker samples such as biofilms, by high-pressure freezing and their effects on SIMS analysis.

5:40pm B+AS+MI+SA-Tua-11 Towards Cryogenic 3D Nano-XRF Imaging of Biological Samples, Axel Rosenhahn, S Stuhr, C Rumeante, T Senibell, T Gorniak, A von Gundlach, J Reinhardt, Ruhr-University Bochum, Germany; Y Yang, P Cloetens, ESF, France; M Grunze, Karlsruhe Institute of Technology (KIT), Germany; J Garrevoet, G Falkenberg, W Schröder, DESY, Germany

Nano probe X-ray fluorescence (nano-XRF) analysis allows spatially resolved imaging with chemical sensitivity. Approaching the diffraction limit at the next generation of storage rings, both, spatial resolution and brilliance are going to be strongly enhanced for nano-XRF experiments. For biological samples, the combination of nano-XRF with cryogenic sample environments allows to understand elemental distributions in cells with minimum preparation artefacts. In addition, the cryo-protected samples provide enhanced resistance against radiation damage, which is particularly important for the high photon densities at modern synchrotron sources. Three different applications of cryo-nano-XRF will be presented. For single melanosomes, the technique enabled us to prove the core-shell organization of the organelles using metals as surrogate markers. As second application, the distribution of metals in single, adherent cells was directly imaged without the requirement of additional markers. Finally, marine adhesives of diatoms were analyzed and the occurrence of metals are linked with the known organic constituents in the EPS of diatoms. In all three cases, the detection of metal distribution has provided a new view on the investigated samples. The cryogenic sample environments proved to be the key to apply synchrotron radiation to all three types of biological samples. The data will also be discussed in relation to the perspectives of new implementations that will enable fast cryo-3D imaging in the future.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 9 - Session SA+AS+HC+SS-Tua

Frontiers of Photoelectron Spectroscopy: Surface & Interface Processes with Variable Depth Probe, High Spatial or Temporal Resolution

Moderators: Geoff Thornton, University College London, Carla Bittencourt, University of Mons, Belgium

2:20pm SA+AS+HC+SS-Tua-1 AVS 2017 Medard W. Welch Award Lecture: Ionic Liquid Surface Science, Hans-Peter Steinrueck; University Erlangen-Nuerenberg, Germany

INVITED

ionic liquids (ILs) are molten salts with a melting point below 100°C. They represent a new class of liquid materials with unique property profiles originating from a complex interplay of Coulombic, hydrogen bonding, and van der Waals interactions of their ions. The enormous variety of cation-anion combinations enables tuning of the physico-chemical properties over a wide range. Functional groups can be implemented in their chemical structure to adapt them for specific tasks - such functionalized ILs are known as 'task-specific ionic liquids'. Applications range from catalysis and organic synthesis to tribology, protective coatings and gate dielectrics. In catalysis, two important concepts are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film, which contains either a homogeneously dissolved transition metal complex for SILP, or which modifies catalytically active surface sites at the support for SCILL. The interface of the IL with the gas phase/vacuum or with the solid support plays an important role. Therefore, knowledge about surface and interface properties and their relation to the chemical structure is of pivotal importance for choosing the right IL for a specific application. In contrast to most other liquids, ionic liquids have a very low vapor pressure, and thus can be studied with the methods of ultrahigh vacuum-based surface science. One particularly powerful method is angle-resolved X-ray photoelectron spectroscopy. Thereby, detailed information on their surface composition, on segregation and enrichment effects, on the dissolution and reactivity of catalytically active metal complexes, on the growth of ultrathin IL-layers, and even on reactions in the liquid phase, can be obtained. Several examples will be discussed illustrating the power of surface science to study this new materials class. Many of the derived conclusions are considered representative for liquid surfaces in general.


3:00pm SA+AS+HC+SS-Tua-3 In Situ Characterization of Semiconductor Nanowire Devices by Nano-Focus X-ray Photoemission Microscopy and Spectroscopy, S McKibbin, Andrea Trojan, S Yngman, Lund University, Sweden; H Sezen, M Amati, L Gregoratti, Elettra-Sincrotrone Trieste, Italy; A Mikkelsen, R Timm, Lund University, Sweden

Il-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. X-ray photoemission spectroscopy (XPS) has been proven highly suitable for studying surface composition and electronic properties of homogeneous NWs [3]. However, in order to better understand NW device performance, it is essential to also investigate NW heterostructures, with nm-scale lateral resolution and during device operation.

Here, we will present nano-focus XPS results from material and doping heterostructures in InP and GaInP NWs intended for photovoltaic application [2]. We used scanning photoemission microscopy (SPM) at the ESCAMicroscopy beamline of the ELETTRA synchrotron, providing a lateral
resolution of about 120 nm, for imaging individual NWs. In addition, we revealed the change in local surface potential across (GaInP) pn-junctions and InP/GaP tunnel junctions, obtained from In 3d, In 4d, and P 2p XP spectra acquired along the heterostructure NW. Electrical contacts were provided to both ends of the investigated NW, allowing to vary the source-drain bias along the NW during SPEM characterization. We will present detailed results on the influence of built-in potential and external forward and backward bias on the surface potential distribution across NW interfaces.

In another approach, we aim at revealing in-situ the interplay of surface chemical composition and local electronic properties. As a model system, we chose InAs NWs consisting of several segments of wurztite and zincblende crystal structure [4]. At the interface between such segments, we confirmed a staggered type-II electronic band alignment, obtained from nano-focus XP spectra along externally biased NWs. After removing the native oxide from the NW surface by atomic hydrogen annealing [4] in the XPS UHV chamber, the same NW instead showed flat-band conditions, which is preferential for electronic application [1]. We will discuss future plans of using the dynamic high pressure option of the ESCAMicroscopy beamline for changing the surface chemistry of NWs while simultaneously investigating them with SPEM and nm-scale spectroscopy.

References


Photons and electrons are two common relaxation products upon X-ray absorption, enabling fluorescence yield and electron yield detections for X-ray absorption spectroscopy (XAS). The ions that are created during the electron yield process are relaxation products too, which are exploited in this study to produce ion yield for XA detection. The ionic currents measured in a liquid cell filled with water or iron(III) nitrate exhibit characteristic O K-edge and Fe L-edge absorption profiles as a function of excitation energy. Application of two electrodes installed in the cell is crucial for obtaining the XA spectra of the liquids behind the membrane. Using a single electrode can only probe the species absorbed on the membrane surface. The ionic-current detection, termed as total ion yield (TIY) in this study, also produces an undistorted Fe L-edge XA spectrum, indicating its promising role as a novel detection method for XAS in liquid cell.

5:00pm SA+AS+HC+SS-Tua-A-9 Non-destructive Depth Profiling of LaAlO₃/SrTiO₃ Interfaces, Conan Weiland, NIST; A Rumaiz, National Synchrotron Light Source II, Brookhaven National Laboratory; G Sterbinsky, Advanced Photon Source, Argonne National Laboratory; J Woicik, NIST

The interface between LaAlO₃ (LAO) and SrTiO₃ (STO) is known to be conducting, even though both LAO and STO are insulators. The interface may also host a variety of interesting phenomena such as a two-dimensional electron gas, ferromagnetism, and superconductivity. Various mechanisms have been proposed to explain the formation of the conductive interface, including the ‘polar catastrophe’, wherein the polar discontinuity at the interface leads to a diverging potential allowing electronic reconstruction, oxygen vacancies at the interface or at the LAO surface, and chemical intermixing, amongst others.

Synchrotron-based variable kinetic energy x-ray photoelectron spectroscopy (VKE-XPS) is a unique and powerful tool to non-destructively probe the chemical and electronic structure of buried interfaces such as that between LAO and STO. Using VKE-XPS, we have analyzed a series of LAO films on STO and have observed compositional variations in the LAO films as a function of depth: Al-enrichment occurs at the LAO surface. Additionally, an electric field was observed in some samples. In this presentation we will discuss the relevance of these results on the formation of conductive LAO/STO interfaces.

5:20pm SA+AS+HC+SS-Tua-A-10 Hard X-ray Photoelectron Spectroscopy Study of the Resistive Switching in Te-based Conductive Bridging Random Access Memories, Munique Kazar Mendes, E Martinez, O Renault, R Cassilhoud, M Bernard, M Veillerot, CEA/Leti-University Grenoble Alpes, France; J Aiblett, Synchrotron SOLEIL, France; N Barrett, SPEC, CEA Saclay - University Paris-Saclay, France

Conductive bridging random access memories (CBRAM) are emerging devices for the next generation of non-volatile memories (NVM) [1]. The CBRAM mechanism is related to ionic transport and electrochemical reactions, which give rise to the formation and dissolution of a conductive filament through the insulating dielectric layer (2). Data storage relies on switching the resistivity between two high (HRS) and low (LRS) resistance states by applying voltage or current pulses. We investigate the electrochemical reactions involved in the switching mechanism of AlO-based CBRAMs with different active electrodes (TiTe and ZrTe) (3). We have used hard X-ray photoelectron spectroscopy to learn about electrochemical reactions involved in the switching mechanism with sufficient depth sensitivity. Photon energies of 6.9, 8.0 and 10.0 keV were chosen to obtain a non-destructive in-depth chemical characterization with varying sampling depths. The XHAXES experiments were performed at the Galaxies beamline (SOLEIL) on As-grown samples, after ex-situ forming (Formed) and after Reset operations. The comparison between these different resistance states shows the role and evolution of the electrode/electrolyte interfaces during electrical biasing. For the Ta/NiTe/AlO/Te stack, results highlight, the reduction of Ti together with alumina oxidation after forming. The sample polarization causes oxygen migration, probably in the O²⁻ form, pushed by the upper negative bias towards the interface between the active electrode and the solid electrolyte (AlO). When reversing the polarity of the applied voltage (Reset operation), we observe Ti reoxidation and alumina reduction, characterizing oxygen migration towards the active TiTe electrode. These results reveal the important role of oxygen migration in the filament formation/dissolution. ToF-SIMS measurements are also performed to get complementary in-depth chemical information. We will finally compare the two active electrodes to investigate the influence of the composition on the switching mechanism.

References

and magnetic and magnetotransport properties of La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films as a function of the oxygen vacancies and films thickness.

6:00pm SA+AS+HC+SS-TuA-12 Synchrotron-Based X-ray Spectroscopy Studies of Inorganic-Organic Hybrid Halide Perovskite Materials Surfaces and Properties, Deidra Hodges, S Shahriar, A Mishra, V Castaneda, V Vidal, M Martinez, N Garcia, J Munoz, J Lopez, University of Texas at El Paso

Recently, the methylammonium lead iodide CH$_3$NH$_3$PbI$_3$ perovskites have attracted a lot of attention as a possible absorber material for thin film solar cells due to their bandgap energy, high optical absorption coefficients and low-cost solution-processing deposition approaches. Methylammonium lead iodide CH$_3$NH$_3$PbI$_3$ perovskite solar cells have evolved with transformative potential with laboratory efficiencies greater than 20%. Perovskite absorber materials are very inexpensive to synthesize and simple to manufacture, making them an extremely commercially viable option. Solar cell efficiencies of devices using these materials have increased from 3.8% in 2009 to a Newport certified 20.1% in 2015, making this the fastest-advancing solar cell technology to date. These devices are known for their high photon absorptivity, tunable large direct band gaps with superior carrier charge transports, and low-cost methods of fabrication. Methylammonium lead tri-iodide CH$_3$NH$_3$PbI$_3$ perovskites thin films and single crystals were prepared for synchrotron-based X-ray spectroscopy studies of the perovskite materials surfaces and properties. The perovskite thin films and single crystals were characterized at the National Synchrotron Light Source (II) (NSLS-II) at Brookhaven National Laboratory (BNL). Synchrotron-radiation-based chemical analysis using X-ray fluorescence (XRF), and X-ray absorption near edge structure (XANES) spectroscopy were performed on samples for detailed analysis into chemical composition, stoichiometry, and material surface properties.
Novel Trends in Synchrotron and FEL-Based Analysis Focus

Topic

Room Central Hall - Session SA-TuP

Synchrotron and FEL-Based Analysis Poster Session

SA-TuP-2 Inelastic Background Analysis using a Reference on Technologically Relevant Samples: Determination of Input Parameters, Charlotte Zborowski, O Renault, CEA/LETI-University Grenoble Alpes, France; A Torres, CEA/LETI-University Grenoble Alpes, France; Y Yamashita, NIMS, Japan; G Grenet, Inl, Ecl, France; S Tougaard, SDU, Denmark

Abstract: Recently, the advent of Hard X-ray Photoelectron Spectroscopy (HAXPES) has enabled to study deeply buried interfaces [1,2]. It was shown that by combining HAXPES with inelastic background analysis [3], structures at a depth >50 nm can be studied. This study was performed on technologically relevant High Electron Mobility Transistors presenting different thicknesses of the Ta/Al electrode on an Al_{0.35}Ga_{0.65}N/AlN/GaN heterostructure. HAXPES was performed at the Spring-8 synchrotron using 8 keV photons. Here, we present a non-destructive solution to get information on deeply buried layers and interfaces. This is a refined analytical method, based on the use of a reference spectrum, for determining the required input parameters, i.e. the inelastic mean free path calculated using the TPP-2M formula and the inelastic scattering cross-section. As the spectra present marked plasmons, after the elastic peaks, we used an average of individual inelastic scattering cross-sections [4], K, which can be determined from Reflection Electron Energy-Loss Spectra. The use of a reference sample gives extra constraints which make the analysis faster to converge towards a more accurate result. The results were determined with the best Ta 3p to corrected spectra calculated with different cross-sections and the resulting in-depth distribution was found with an accuracy better than 5% and in good agreement with the TEM results. We have also successfully used this technique to study structures at a depth >70 nm.

References


Part of this work was performed at the Nanocharacterization Platform of CEA-MINATEC. NIMS and Spring-8 are acknowledged for providing beamtime and the staff of the BL15-XU beamline for their assistance during the experiment.


During the past decade, increased attention has been shown to hard X-rays in the photoelectron spectroscopy field. This is mainly due to the increased information depth enabled by the higher photon energies. Such bulk sensitive measurements could previously only be performed at dedicated synchrotron radiation facilities. The beam lines providing this type of radiation are heavily booked, so access to the experimental setups is thus limited.

We now present a novel product featuring a monochromized X-ray source giving out Ga Ka radiation at 9.25 keV and an eight acceptance angle hemispherical electron analyzer, both combined on a simple to use vacuum system. The base system can be easily customized by adding separate modules such as a MBE- or preparation chamber or a glove box. With this novel base system, a new set of possible experiments opens up in the home laboratory: investigations of buried interfaces, in operando devices, real world samples, etc. Such samples or conditions have previously been unattainable with the limited information depth of traditional XPS.

At the heart of the system is a liquid jet of a molten Ga-rich alloy. Electrons which are accelerated into this jet generate an intense Ga Ka radiation. These X-rays are monochromized and refocused using an ellipsoidal mirror in a Rowland geometry. The small spot size of 20 µm provided by the liquid jet source is maintained throughout the passing of the monochromator and only slightly broadened to about 50 µm. The photon energy width is targeted at 0.5 eV, suitable for the typical intrinsic core level width at the relatively high photon energy. In order to allow for easy adjustment of the X-ray focal point relative to the electron analyzer, the entire assembly of monochromator and source can be moved down to a precision of a few micrometers. The hemispherical electron analyzer is configured for high kinetic energies allowing for detection of the full energy range the source provides, a large acceptance angle of +/-30 degrees.

We present prototype data taken from polycrystalline gold and silicon wafers with a surface layer of silicon dioxide with a controlled thickness.

SA-TuP-4 Vacuum System of the ESS Cold Linac, Update on Design and Status, Fabio Ravelli, S Scolari, M Ferreira, European Spallation Source ERIK, Sweden

The European Spallation Source, under construction in Lund (Sweden), is a neutron source based on a 5 MWatt super-conducting linear accelerator. The ultimate goal of ESS is to be the brightest neutron scattering facility and to enable novel science in many fields, such as biology research, environmental technologies and fundamental physics.

After a brief description of the superconducting Linac, the talk focuses on the vacuum design of the Warm Units that give continuity to the beam line environment between adjoining cryomodules [1]. As the use of N evaporable Getter and Sputter Ion pump combinations is under evaluation, a campaign of measurements on particles generated during operation (activation - regeneration - pumping) by two different models of combination pump has been performed; the results of these tests are discussed. Finally, some insights about particle free installation tooling [2] are presented.

[1] ESS Vacuum System Status, Dr. Marcelo J. Ferreira, ESS Vacuum System Section Leader, IVC-20, August 21-26, 2016, Busan, Korea
[2] Particle Free Installation of Warm Linac Units at ESS F. Ravelli and M. J. Ferreira, 2016 CAS Accelerator School, October 2-14, 2016, Budapest, Hungary
Beyond Traditional Surface Analysis: Pushing the Limits

Moderators: Svitlana Pylypenko, Colorado School of Mines, Paul Vlasak, The Dow Chemical Company

8:00 am AS+B+Mi+NS+SA+SS-WeM-1 Photolysis of Pyruvic Acid in Aqueous Solution as a Source of Aqueous Secondary Organic Aerosol, Yoo Fu, X Yu, F Zhang, Z Zhu, Pacific Northwest National Laboratory; J Chen, Fudan University; X Yu, Pacific Northwest National Laboratory

Pyruvic acid are found in fogs, aerosols and clouds. The sunlight driven reaction pathways of pyruvic acid in the aqueous phase are more elusive compared to its well-known gas phase chemistry. Aqueous solutions containing pyruvic acid in a microchannel after different UV photolysis times up to 8 hours have been studied by in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) for the first time. Both positive and negative ion mode mass spectra provided complementary information of the photochemical aging products at the solution surface. Compared with previous results using bulk approaches (i.e., NMR, ESI-MS), our unique liquid surface molecular imaging enables the observation of photochemical products of pyruvic acid at the aqueous solution surface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartraric acid), and water clusters (i.e., (H2O)4H+, (H2O)3OH−) with submicrometer spatial resolution. Spectral principal component analysis is used to determine similarities and differences among various photochemical aging samples. SIMS secondary ion chemical mapping permits visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant shown in the chemical spatial mapping with increased photolysis time. In situ molecular imaging of the pyruvic acid aqueous solution provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

8:20 am AS+B+Mi+NS+SA+SS-WeM-2 XPS Depth Profiling of SrTiO3 and HfO2 with Small Argon Clusters, Christopher Deeks, Thermo Fisher Scientific, UK; M Baker, University of Surrey, UK; P Mack, Thermo Fisher Scientific, UK

Metal oxides are employed in a wide variety of functional applications. There is currently strong technological interest in strontium titanate (SrTiO3) and hafnium oxide (HfO2) due to their specific band gaps and high dielectric constants. SrTiO3 is being studied for use in photocaltalysis, energy storage and electronic sensors, whilst HfO2 is widely employed for optical coatings and optoelectronic device applications. Both materials are regularly deposited as thin films and doped to optimise their properties for the application. An accurate determination of the thin film composition is paramount to the understanding and optimisation of device performance. In this work, thin films of SrTiO3 and HfO2 have been deposited onto silicon substrates and XPS depth profiles have been performed through the thin films using both monatomic and cluster argon ion bombardment. The monatomic Ar+ profiles were performed using an incident ion energy of 500 eV and the gas cluster ion beam (MAGGIS) profiles were recorded using 8 keV Ar300+ and 8 keV Ar350+ for SrTiO3 and HfO2 respectively. For HfO2 the optimum results were found when the MAGGIS ion beam was incident upon the sample at a glancing angle. These MAGGIS conditions yielded excellent retention of the original SrTiO3 and HfO2 stoichiometry during the profile, with no evidence of preferential sputtering or ion beam induced reduction. Using 500 eV Ar+, however, resulted in the preferential sputtering of oxygen leading to the presence of sub-oxide states in the XPS spectra. In contrast, Hf and Ti XPS spectra. The depth resolution was similar between the monatomic and cluster ion depth profiles for both thin film materials. Using the same incident ion beam angle, the etch rate for 8 keV Ar350+ was only 2.5 times lower than that for 500 eV Ar+. The results will be discussed in the light of known ion beam effects when sputtering metal oxide materials.

8:40 am AS+B+Mi+NS+SA+SS-WeM-3 Surface Analysis of Intact Biomolecules: the Bigger They Are the Harder They Fly, Nina Oprinc Potocnik, R Heeren, Maastricht University, The Netherlands

The use of focused ion beams for desorption and ionization of surface molecules in SIMS affords for this notable spatial resolution over, for example, laser-based MS approaches such as Matrix Assisted Laser Desorption Ionisation (MALDI). However, the excessive energy of the primary ions limits the method to the detection of elements, fragmented molecules and small intact molecular species. This consequently points at the method’s major drawback, which is the difficulty to ionize and detect larger, intact molecular species such as peptides and proteins with great sensitivity. Over the last years, this method has been pushing the area away by redirecting focus into biomedical applications. Tissue sections and cell imaging has become common practice in research labs all over the world. Now, abundant lipids and small peptides can be studied with different sample surface modifications, where the upper most layer of the surface is sputter coated with a thin layer of metal (M(Al) SIMS – metal-assisted SIMS) or covered with the matrix (ME-SIMS). In both cases the sputtering efficiency and the secondary molecular yield have increased. Here, we studied how ME-SIMS can influence the ionization efficiency of desorbed intact molecules in comparison to MALDI.

First, we imaged mammalian tissue sections that were subjected to a variety of different matrices using a home-built sublimation chamber. Matrix sublimation produces small, homogenous crystal sizes, without the need for solvents that delocalize molecular species. The same or consecutive sections were subsequently analyzed by FTICR-SIMS, to accurately identify the enhanced molecular species of interest, specifically intact lipids and metabolites, and by the PHI nano-TOF II for high lateral resolution images and confident identification of said species with tandem MS. Second, de-novo peptide sequencing was performed on endogenous neuropeptides directly from a pituitary gland. Careful sample preparation and the capability of using a 1 Da mass isolation window of the precursor ion followed by a collision-induced dissociation (CID) at 1.5 keV in an activation cell with argon gas enables the molecules to be fragmented in a specific pattern. Neuropeptides up to m/z 2000 were detected and sequenced from the posterior lobe. Further on, we applied it for the characterization of tryptically digested peptides from a variety of tissue sections investigating the applicability to bottom-up proteomics.

2000 were detected and sequenced from the posterior lobe. Further on, we applied it for the characterization of tryptically digested peptides from a variety of tissue sections investigating the applicability to bottom-up proteomics.

9:00 am AS+B+Mi+NS+SA+SS-WeM-4 Hydrogen/Deuterium Exchange Using Vapor Phase D2O to Enhance SIMS Characterizations, Paul Vlasak, The Dow Chemical Company

Hydrogen/Deuterium exchange of labile hydrogens is a well-known water solution-based phenomenon that has in recent years seen extensive use in the area of protein characterization. This presentation will demonstrate a method to accomplish vapor phase hydrogen/deuterium exchange of solid sample surfaces prior to analysis by SIMS. In many cases, it is not desirable to expose the sample to liquid solvent due to the possibility of dissolving and rearranging or removing surface species of interest. In contrast, the effect of vapor phase D2O exposure is similar to typical exposures of the sample to humid room air.

The described method is simple and inexpensive in comparison with synthetic isotopic labeling studies. However, it is expected that only the sufficiently labile and sterically accessible H atoms can be tagged, typically those bound to N, O, or S. Possible benefits of this method include isomer differentiation, elucidation of fragmentation pathways, fundamental studies of ionization, differentiation of sterically or otherwise protected vs. unprotected functional groups, and determination of water diffusion or permeability in solid materials.

9:40 am AS+B+Mi+NS+SA+SS-WeM-6 Fragmentation and Backscattering of Large Ar+ Clusters as a Probe of Polymer Glass Transition, C Poleuxinis, Université Catholique de Louvain, Belgium; V Cristaudo, Université Catholique de Louvain, Belgium; Arnaud Delcorte, Université Catholique de Louvain, Belgium

Gas cluster ion beams (GCIB) have become the standard sources for molecular depth-profiling of organic materials with secondary ion mass spectrometry (SIMS) [1] and X-ray photoelectron spectroscopy (XPS). Since 2009, a number of experimental and theoretical studies were devoted to the investigation of the effects of energy, nuclearity and incidence angle of the Ar clusters on the energy deposition, fragmentation and molecular emission induced in organic solids [2-4]. Recently, Mochiji et al. reported that the backscattered Ar+ clusters observed in the SIMS spectra of pure metal surfaces provide information on the mechanical properties of the surfaces analysed by GCIB [5]. They correlated the ratio of Ar+ to the sum of Ar+ clusters intensities with the impulsive stress caused by the impact, a parameter directly linked to the elastic modulus of the material.

Here, the intensity variations of the backscattered Ar+ clusters are studied as a function of temperature for a series of thermoplastic polymers: high
molecular weight polydisperse polysobutylene and polybutadiene, polystyrene (Standard; Mw = 4000) and polymethyl methacrylate (Standards; Mw = 2000 and 150000). For all these polymers, our results show a transition of the intensity ratio Arz/(Arz+Ar+)/ when the temperature is scanned from -120 °C to +125 °C. This transition generally spans over a few tens of degrees and the temperature of the inflexion point of each curve is very close to the glass transition temperature (Tg) reported for the considered polymer. Due to the surface sensitivity of the cluster backscattering process (a few nanometers as indicated by molecular dynamics simulations [4]), the presented analysis could provide a new method to specifically evaluate the surface Tg of polymers, with the same lateral resolution as the gas cluster beam. The results are discussed from the point of view of the structure and mechanics of polymers.


11:00am AS+Bi+M+NS+SA+SS-WeM-10 Evolution of the Bi Cluster LMIS as a Universal Source for High Performance SIMS Analysis, Felix Kollmer1,
ION-TOF GmbH, Germany

INVITED

In 1987 Appelhans and co-workers performed a groundbreaking experiment. They bombarded a polymer surface with a neutral SF6 beam in order to avoid charging effects on insulators. By coincidence they discovered that the SF6 beam is doing an excellent job of producing secondary ions...it is unexpectedly efficient at sputtering secondary ions from these polymer surfaces [1].

In the following years the bombardment of organic surfaces with clusters was investigated by many research groups. The lateral resolution of the applied beams was rather low since the focus at this time was clearly on the fundamentals of the ion solid interaction and the secondary ion generation. However, as early as 1991 Benguerba applied an Au cluster liquid metal ion source (LMIS) for a fundamental study of phenylalanine [2].

At the beginning of the millennium the Au cluster LMIS became commercially available for TOF-SIMS instrumentation. This led to a wider application in the SIMS community and to a further improved performance. However, the cluster sources remained an additional option for the SIMS instruments especially since the low cluster currents did not allow the replacement of the reference Ga LMIS for many applications.

With the introduction of a LMIS operated with Bi this changed fundamentally [3]. Roughly 50% of the beam consists of clusters and 50% are emitted as mono-atomic Bi species. This ensures a large flexibility for the analysis of inorganic as well as organic surfaces. Moreover, an uncompromised performance in terms of lateral and mass resolution is achieved, even with cluster beams, and a lateral resolution in the sub 20 nm range has been demonstrated with Bi ions [4].

Today, the Bi LMIS is used as the standard analysis source on more than 250 TOF-SIMS instruments for all kinds of applications. In combination with a massive cluster beam that is applied for the erosion of the sample (e.g. Ar) even depth profiling or 3D analysis of organic samples is possible.

In this contribution, we will have a retrospective look at the development of high performance cluster SIMS. Besides fundamental capabilities of the Bi LMIS and the secondary ion generation we will discuss milestones of the application as well.

Wednesday Morning, November 1, 2017

Demonstrate that the coupling of ToF-SIMS and electrochemistry has great potential to molecularly elucidate reaction mechanisms in the oxidative metabolism, pharmaceutical intoxication, and cell toxicity.

References


Magnetic Interfaces and Nanostructures Division
Room 11 - Session MI+SA-WeM

Controlling the Magnetism in Oxides and Multiferroics and Chirality in Spin Transport and Magnetism (cont.)

Moderator: Valeria Lauter, Oak Ridge National Laboratory

8:20am MI+SA-WeM-2 Integrated Magnetics and Multiferroics for Compact and Power Efficient Sensing, Power, RF, Microwave and mm-Wave Tunable Electronics, Nian Sun, Northeastern University

INVITED

The coexistence of electric polarization and magnetization in multiferroic materials provides great opportunities for realizing magnetoelectric coupling, including electric field control of magnetism, or vice versa, through a strain mediated magnetoelectric coupling in layered magnetic/ferroelectric/multiferroic heterostructures [3-9]. Magnetoelastic coupling has been the enabling factor for different multiferroic devices, which however has been elusive, particularly at RF/microwave frequencies. In this presentation, I will cover the most recent progress on new integrated multiferroic materials and devices for sensing, and from power to mm-wave electronics. Specifically, we will introduce magnetoelectric multiferroic materials, and their applications in different devices, including: (1) ultra-sensitive magnetometers based on RF NEMS magnetoelectric sensors with picoTesla sensitivity for DC and AC magnetic fields, which are the best room temperature nano-scale magnetometers; (2) novel ultra-compact multiferroic antennas immune from ground plane effect with 200μm × 1μm or 1/600 in size, -18dBι gain, self-biased operation and 17% voltage tunable operation frequency; and (3) novel GHz magnetic and multiferroic inductors with a wide operation frequency range of 0.3~3GHz, and a high quality factor of close to 20, and a magnetic field to switch the magnetization orientation of the underlying ferromagnetic substrate. Here, the latter process is modulated with an external magnetic field to switch the magnetization orientation of the underlying ferromagnetic substrate.

Reference:


9:20am MI+SA-WeM-5 Controlling Spin Selectivity in Photoinduced Charge Transfer through Patterned DNA Microarrays, John Abendroth1, N Nakatsuka, M Ye, D Stemer, University of California at Los Angeles; D Kim, E Fullerton, University of California at San Diego; A Andrews, P Weiss, University of California at Los Angeles

Understanding spin-selective interactions between electrons and chiral molecules is critical to elucidating the prospective significance of electron spin in biological processes. We report the visualization of spin-dependent charge transport in microscale-patterned, self-assembled monolayers of double-stranded DNA on ferromagnetic substrates using fluorescence microscopy. Patterned DNA arrays provide background regions in every measurement to quantify the substrate magnetization-dependent fluorescence due to the chiral-induced spin selectivity effect. Fluorescence quenching of photoexcited dye molecules bound within DNA duplexes is dependent upon the rate of charge separation/recombination upon photoexcitation and efficiency of DNA-mediated charge transfer to the surface. Here, the latter process is modulated with an external magnetic field to switch the magnetization orientation of the underlying ferromagnetic substrates. Using this experimental technique, we are investigating molecular parameters that can be manipulated to influence the magnitude of the spin selectivity effect in DNA arrays to assess candidly the potential of chiral assemblies for organic spintronics. In particular, we are monitoring the influence of heavy metal species that are incorporated predictably within DNA duplexes to change the strength of molecular spin-orbit coupling as a result of the heavy atom effect.

References:


1 Falicov Student Award Finalist
Enantiomer-dependent Spin Orientation in Photoelectron Transmission through Heptahelicene Molecules, Matthias Kettner, D Nüenberger, University of Münster, Germany; J Seibel, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; H Zacharias, University of Münster, Germany; R Ernst, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland.

The interaction of electrons with helical molecules attains growing interest due to a spin selectivity in electron transmission. Experiments on self-assembled monolayers of double stranded DNA [1] and oligopeptides [2,3] indicated a very efficient spin filtering behavior of the molecules at room temperature.

In present experiments enantiopure M- and P-heptahelicene molecules are evaporated onto different metal single crystal surfaces. The molecules arrange themselves to a highly ordered monolayer [4,5]. Samples are then irradiated with \( \lambda = 213\text{nm} \) laser radiation to generate photoelectrons from the substrate. These electrons are transmitted through the heptahelicene layer and analyzed with regard to their average longitudinal spin orientation by Mott scattering. The sign of the spin polarization depends on the helicity of the enantiomer. The effect of the heptahelicene on the spin orientation seems to be independent on the substrate.

References

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 9 - Session SA+2D+AC+MI-WeM
Recent Advances of Diffracting/Scattering and Spectroscopic Methods for Correlated and 2D Materials
Moderators: Hans-Peter Steinrück, University Erlangen-Nürnberg, Germany, Kristina Edström, Uppsala University, Sweden

In heterogeneous catalysis, reactants adsorbed on surfaces are converted to products, which eventually desorb via various intermediates. The transition state separates reactants and intermediates from products and the free energy required to reach it determines the kinetics of an elementary chemical reaction. Many surface reaction intermediates are, however, transient species with a short residence time and the population of species in the transition state region is near-zero making their observation a challenge during steady state conditions. Ultrafast pump-probe techniques have, however, opened up opportunities by promoting a sufficient population of molecules in transient states to allow detection on short time scales. Here recent results on probing chemical reactions on surfaces using X-ray free-electron lasers LCLS (Linac Coherent Light Source) at SLAC National Accelerator Laboratory will be presented. Four examples will be shown: CO desorption, Oxygen activation, CO oxidation and CO hydrogenation on Ru(0001). We demonstrate that both transient intermediates and the transition state region can be detected in surface chemical reactions.

8:40am SA+2D+AC+MI-WeM-3 New Generation RIXS of 3d-TM Oxides, Giacomo Giringhelli, Politecnico Milano, Italy

Invited
Resonant inelastic soft x-ray scattering huge potential is quickly becoming reality. RIXS is element and site selective, like x-ray absorption spectroscopy. It is momentum resolved, like x-ray diffraction. And it probes several kinds of excitations at a time, from charge transfer and electron-hole pair generation, to orbital (dd or ff) excitations, to spin waves and lattice modes, unlike any other energy loss spectroscopy. Moreover, the elastic component of the spectra carries information on commensurate and incommensurate orders, such as charge density waves (CDW) and orbital order. The ERIXS endstation at the ID32 beam line of the ESRF is the founder of a new generation of RIXS instruments capable of exploiting all the strongpoints of this technique, thanks to the very high resolving power (30,000 at 1 keV), the diffractometer-like manipulator and the full control of photon polarization provided by the combination of the APPLE II source and the polarimeter on the analyzer.

I will review some of the results obtained in the first year of operations of ID32, with a special focus on cuprate superconductors studied at the Cu L_2 edge. High resolution RIXS has been used to determine the relation between crystal structure and the extent of hopping integrals in parent compounds, revealing why apical oxygens are detrimental to superconductivity [1]. Ultra-high resolution RIXS has provided a direct measurement of the momentum-dependent electron phonon coupling in undoped and superconducting samples, and has revealed new collective modes related to charge density waves (CDW) in underdoped Bi2212. Polarization analysis has definitively demonstrated the spin-flip character of the mid-IR spectral region in superconducting compounds. And the quasi-elastic part of RIXS spectra has brought new evidence of the universality of charge ordering phenomena in cuprates, including striped cuprates [2] and single layer Bi2201. Finally the feasibility of high resolution RIXS in standing wave geometry has been successfully demonstrated, adding depth control on this bulk sensitive technique.


9:20am SA+2D+AC+MI-WeM-5 Resonant Inelastic X-ray Scattering on Low-Dimensional Correlated Transition Metal Oxides and Oxide Heterostructures, Thorsten Schmitt, Paul Scherrer Institut, Switzerland

Invited
Resonant inelastic X-ray scattering (RIXS) is a powerful bulk-sensitive photon-in / photon-out spectroscopic probe of the electronic structure of condensed matter with atomic and orbital sensitivity. It is a unique tool for studying excitations from the electronic ground state in correlated transition-metal oxides, being directly sensitive to lattice-, charge-, orbital- and spin-degrees of freedom. In this talk, we report RIXS investigations of the LaTiO_x layers in LaTiO_3/(LaAlO_3)_x superlattices undergoing a transition from Ti^{4+} to Ti^{3+} oxidation state upon reducing n and thickness as well as temperature-driven metal-insulator transitions in thin films of CaVO_3, (LaTiO_3)/(LaAlO_3) superlattices (SL) composed of a band-insulator (LaAlO_3) and a Mott-insulator (LaTiO_3) present an enhanced insulating character when n is reduced. We prepared a set of SLs (n=10, 5 and 2 unit cells) and investigated these with X-ray absorption spectroscopy (XAS) and RIXS. XAS shows a clear change in the Ti valence going progressively from the...
nominal Ti\(^{3+}\) (3d\(^{1}\), n=10 u.c.) for bulk LaTiO\(_3\) to an almost pure Ti\(^{4+}\) (3d\(^{2}\), n=2 u.c.). RIXS reveals two spectral developments when reducing the LaTiO\(_3\) thickness n: 1) reduction of intra-t\(_{2g}\) / intra-e\(_{g}\) splitting and increase of t\(_{2g}\) to e\(_{g}\) separation and 2) increase of the charge transfer excitation spectral weight. The changes in the energy of the orbital levels observed as a function of n reveal a clear change of the local TiO\(_2\) distortion. We suggest that an inverse Jahn-Teller effect, inducing the octahedra to assume higher symmetry, is responsible for the observed orbital energy shifts. This peculiar effect is partially caused by strain, triggering a 3d\(^{1}\) → 3d\(^{0}\) electron transition at the interfacial Ti sites.

Bulk CaVO\(_3\) is a correlated paramagnetic metal. Thin films of CaVO\(_3\) undergo a metal-insulator transition (MIT) when the thickness is reduced below ca. 20 u.c.. Our XAS and RIXS measurements at the V L-edge across this dimensionality driven MIT in CaVO\(_3\) reveal a large transfer of spectral weight from fluorescent to Raman modes upon entering the insulating state. We observe a large reduction in the charge excitation bandwidth and V-O covalence across the thickness and temperature-driven MIT. Further analysis of the charge modes suggests a bandwidth-controlled MIT, assisted by the presence of strong correlations.

11:00am SA+2D+AC+MI-WeM-10 Doping of Graphene Exploited with Spectromicroscopy, Carla Bittencourt, University of Mons, Belgium

INVITED

Limitations in characterisation and theoretical modelling tools have been a major obstacle for the engineering of novel functional materials with properties enhanced by their nanoscale morphology, because detailed understanding of the structure–property–operando relationships are required. In this perspective technology has entered in a period of convergence between theory and characterisation tools, traditional spectroscopic techniques are being combined with microscopy to characterise individual nano-objects. In this context advances in the design and fabrication of x-ray focusing systems allow modifying conventional X-ray spectoscopies using synchrotron light to be used to study individual nanostructures and selected regions of a nanoscale sample. These spectroscopies are amongst the most powerful tools in material science providing elemental, electronic, structural and chemical information. Recent trends include in-operando analysis of individual nanostructures.

In my talk I will report recent results obtained using spectromicroscopy techniques to study the doping of suspended graphene flakes. The nitrogen doping of suspended graphene was performed via ion implantation. We will show that inclusion of up to 20 at.% nitrogen can be reached, while maintaining a sp\(^3\)-network. The evolution of nitrogen species: pyridinic, graphitic, and pyrrolic, at different doping stages and annealing temperatures is observed by scanning X-ray photoelectron microscopy (SPEM). Variations in the ratio between sp\(^3\) nitrogen species is observed for increasing treatment time; thermally heating the doped carbon nanostructure results in quenching of the sp\(^3\) component, suggesting the graphitic nitrogen as the most thermal stable species. The effect of the interaction of molecular oxygen with nitrogen doped graphene will be discussed.

11:40am SA+2D+AC+MI-WeM-12 Multi-modal and Multi-dimensional Synchrotron Investigation of Functional Materials, Karen Chen-Wiegart, Stony Brook University/Brookhaven National Laboratory

INVITED

Multi-modal and multi-dimensional characterization at synchrotrons can provide unprecedented information for complex, heterogeneous materials system. A multi-modal approach combines multiple synchrotron techniques to gain complementary information. Furthermore, with imaging techniques specifically, multi-dimensional imaging includes techniques such as tomography, spectoscopic microscopy, or in situ/operando imaging. These capabilities are particularly powerful when used to study complex structures with morphological and chemical heterogeneity. This talk will address the applications in energy storage and conversion materials, including Li-ion batteries, Li-S batteries, and solid-oxide fuel cells. Other examples, including nano/meso-porous metals, cultural heritage and surface treatment on metals will also be briefly discussed.
Applied Surface Science Division
Room 13 - Session AS+2D+NS+SA-WeA

2D, 3D and nD Imaging of Surfaces, Buried Interfaces and Nanostructures

Moderators: Michael Brumbach, Sandia National Laboratories, Kathryn Lloyd, DuPont

2:20pm AS+2D+NS+SA-WeA-1 Laser-SNMS Imaging of Organic and Biological Systems in Two and Three Dimensions, Bonnie June Tyler, A Pelster, M Heeger, H Arlinghaus, Universität Münster, Germany

The introduction of commercial large argon gas cluster ion sputter sources has enabled routine molecular depth profiling and 3D imaging of organic materials with ToF-SIMS. 3D molecular imaging has been demonstrated for a wide variety of organic and biological systems. Despite these advances, sensitivity and quantitation continue to limit applications of the technique for many important systems such as pharmaceuticals. Laser post-ionization of sputtered neutral species is one potential solution to the problems of both low sensitivity and matrix effects.

In this work, we have compared ToF-SIMS and Laser-SNMS for 2D and 3D imaging of several organic systems, including biological samples, pharmaceuticals, and polymeric materials [1-3]. Sample analysis and sputtering were performed using combinations of Bi+, and Ar+ ions. Laser post-ionization was performed using either a 157 nm excimer laser or a 195 nm excimer laser. For organic molecules, superior results are obtained using the shorter wavelength laser at lower power density whereas higher power density with the longer wavelength laser is superior for elemental analysis. Increases in ion yield of as much as 4 orders of magnitude have been observed for both elemental and molecular species.

ToF-SIMS and Laser-SNMS show complementary strengths. For high intensity ion signals, ToF-SIMS allows for faster data acquisition. Laser-SNMS, on the other hand, reduces artefacts from topography and matrix effects and enhances measurement efficiency. Higher efficiency reduces the amount of matter that must be sputtered to obtain a given signal, which facilitates measurement of lower concentrations with higher ultimate spatial resolution.


2:40pm AS+2D+NS+SA-WeA-2 Distribution of Surfactants and Polymer in a Coating using GCIB-SIMS, Michaeleen Pacholski, Z Qu, W Ouyang, The Dow Chemical Company

Water-based coatings are commonly composed of a latex polymer with additional formulation ingredients such as surfactants, defoamers, etc. The distribution of the additives can have a large role in product performance affecting properties such as adhesion, gloss, water whitening, cohesion, etc. Using GCIB-SIMS profiling the distribution of the additives throughout a film can be shown to relate to the particle size and expected film formation theoretical results. The data from this study show, for the first time, that polymer, surfactant and salts can be monitored as a function of film depth with superior sensitivity and specificity to previous literature studies.

3:00pm AS+2D+NS+SA-WeA-3 Correlation of Morphological and Hyperspectral Characterization Techniques for NANOelectric and Energy Applications, Jean-Paul Barnes, A Priebe, G Goret, I Mouton, A Grenier, G Audoit, P Bleuet, Y Mazel, E Nolot, Univ. Grenoble Alpes, CEA, LETI, France; S Legendre, A Tempez, Horiba France S.à.r.l., France; R Estivill, M Juhel, STMicroelectronics, France; S Dugugy, F Vurpillot, D Blavette, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, Groupe de Physique des Matériaux, France

INVITED

The integration of a growing variety of materials in increasingly complex structures drives the need to correlate characterization techniques. In this presentation we will discuss the advantages of correlating pairs of techniques such as focused ion beam-time of-flight-secondary ion mass spectrometry (FIB-TOF-SIMS) and X-ray computed nanotomography (CNT); atom probe tomography (APT) and electron tomography (ET); and TOF-SIMS depth profiling and plasma profiling time-of-flight mass spectrometry (PPTOFMS).

FIB-TOF-SIMS tomography extends the capacity of TOF-SIMS instruments to analyze large heterogeneous samples of several tens of microns in size as well as porous samples or those with strong surface topography. Standard depth profiling is often not possible as the depth scale information is rapidly lost in such samples. Examples include copper pillars used in 3-D integration in nanoelectronics and solid oxide fuel cells (SOFCs) which have a complex porous multilayer (sandwich) structure. Whilst FIB-TOF-SIMS provides unique information on the sample chemical composition, there may be morphological artefacts such as curving. These may be identified and corrected by analyzing the sample beforehand by X-ray CNT in an SEM. We have developed a method to analyze the same object by both techniques by using novel sample preparation protocols [1].

The correlation of morphological with hyperspectral data can also be applied to APT and ET. APT is increasingly used for the analysis of semiconductor devices because of its unique ability to measure composition in 3D at the atomic scale with high sensitivity. However the APT data sets are often distorted and care must be taken in quantifying composition. The morphological information obtained from analyzing the APT tip beforehand by ET can be used to optimize the parameters when reconstructing the APT data.

PPTOFMS is a rapid depth profiling technique that uses a plasma to etch away the sample and analyze the composition as a function of depth. Unlike SIMS based techniques, the ionization takes place in the plasma and the ratio of ions extracted from the plasma is directly representative (within a factor of 2-3) of the sputtered sample composition. However, the sensitivity and depth resolution are worse than for TOF-SIMS. Combining PPTOFMS with TOF-SIMS depth profiling enables the standard-free quantification and rapid sample screening capabilities of the PPTOFMS to be combined with the sensitivity and high depth and lateral resolution of TOF-SIMS [3].


INVITED

There is an increasing demand for characterization of materials for nuclear reactors with advanced microscopy techniques. Intelligent materials selection requires a fundamental mechanistic understanding of environmental and irradiation damage processes at the nanoscale.

Current and future nuclear power generating systems require materials that can withstand extreme environments. Long-term resistance to environmental degradation is critical for light water reactors as evidenced by stress corrosion cracking concerns in structural alloys for both primary and secondary systems. Resistance to radiation damage further challenges material selection in current and advanced reactors with unique issues for plasma facing components in tokamak-style fusion energy systems where materials must tolerate extended neutron (14 MeV) and He+ ion (3.5 MeV) irradiation at extreme temperatures (up to 1300 K). Accumulation of metallic fission products in LWR fuels may cause cracking and has been linked to cladding erosion.

2D analytical electron microscopy techniques have and continue to provide key insights into the evolution of local microstructure and chemistry. More recently, these traditional 2D imaging techniques have been complemented by novel 3D imaging methods, including serial sectioning using a focused ion beam, electron tomography and atom probe tomography. When paired with 2D imaging methods, the 3D microscopy provides deeper insights into the hierarchy of the degradation and damage processes, improved statistical relevance and a greater sensitivity to highly localized effects that were not apparent from 2D imaging alone. Going one step further, dynamic processes (such as oxidation and vacancy injection) can be directly imaged by in situ and operando techniques in transmission electron microscopy. Each technique has its own set of strengths and weaknesses, and in this talk we will emphasize how combining these complementary techniques provides a more comprehensive understanding of material degradation than could be obtained from any individual imaging method.

5:00pm AS+2D+NS+SA-WeA-9 XPS Spectroscopic Imaging of 2D Materials, Olivier Renault, CEA-Leti, France; H Kim, EPFL, France; D Ferrah, UCI, France; N Fairley, Casa Software, France; M Goy, CEA-Leti, France; M Frigniaux, UVSQ, France; A Kis, EPFL, France

The recent advent of two dimensional semi-conducting materials of the post-graphene era, such as transition-metal dichalcogenides (TMDs- such
5:20pm AS+2D+NS+SA-Wea-10 Carboxylic Acid Headgroups – Towards a New Standard in SAMs, Anna Krzykawska, Jagiellonian University, Poland; J Ossowski, T Zaba, P Cyganik, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) prepared from biphenyl-substituted molecules chemisorbed on the Ag(111) substrate via an -SH or -COOH headgroup were characterized using scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRRAS), and X-ray photoelectron spectroscopy (XPS). The objective of this work was to determine which of these headgroups, -SH or -COOH, will provide better 2D ordered SAMs. Importantly, to make such comparison valuable, i.e., to correlate the reduction in the concentration of surface defects with the particular headgroup, we need to compare the two systems, which are chemical analogues, and it would be desired that both systems form SAMs of similar packing density. Only under such conditions can the difference in intermolecular interactions in both systems be minimized to determine the role of headgroup bonding to the substrate in the 2D structural ordering of the anchoring SAMs. Our results obtained for monolayers meeting the above criteria show that SAMs with carboxylic headgroups can form, at room temperature and within a very short time of just a few minutes well-ordered 2D structures on Ag(111) with surprisingly large domains. In contrast, the thiol analogue formed at the same temperature reveals poor 2D ordering, with approximately 30 times smaller domains. Importantly, this pronounced difference in 2D ordering is observed despite the approximately 30 times longer incubation process of the thiol analogue. We also demonstrate that formation of the thiol analogue at elevated solution temperature (60°C) can significantly increase the size of its domains, which is, however, still approximately 5 times smaller in comparison to the carboxylic analogue formed at room temperature. Moreover, the structure of the carboxylic analogue on Ag(111) also shows better 2D order compared with the former data obtained for the thiol analogue SAMs formed on the Au(111) substrate at room temperature. Only the formation of the thiol analogue SAMs at elevated solution temperature (60°C) on the Au(111) substrate with 300 times longer formation time provides comparable 2D ordering to that obtained at the room temperature for the carboxylic analogue SAMs on the Ag(111) substrate.

Our results indicate, therefore, that SAMs based on carboxylic head group can be considered an interesting alternative for the current standard based on the sulfur headgroups, particularly when 2D ordering, SAM fabrication time and stability in the ambient conditions are of great importance.

References


Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 24 - Session HC+SA+SS-WeA
Bridging Gaps in Heterogeneously-Catalyzed Reactions
Moderator: Yu Lei, University of Alabama in Huntsville

2:20pm HC+SA+SS-WeA-1 Oxygen Reduction Reaction Activity for Pt/Co/Pt(111) and Pt/Co-N/Pt(111) Model Catalyst Surfaces Fabricated by Arc- plasma Depositions, S Kaneko, R Myoichi, S Takahashi, N Todoroki, Toshimasa Wodayama, Graduate School of Environmental Studies, Tohoku University, Japan; T Tanabe, Graduate School of Engineering, Tohoku University, Japan

Comprehensive understanding of oxygen reduction reaction (ORR) activity enhancement mechanisms for Pt-based alloy (Pt-M) catalysts is a key for developing highly-efficient, low-Pt-loading cathode catalysts for polymer electrolyte fuel cell. To clarify the effects of the alloy surface structures (e.g., Pt shell atomic arrangements, Pt/M ratio etc.) on activity and durability, a number of studies have been performed. We have, thus, investigated ORR properties for the well-defined Pt-based bimetallic single crystal surface alloys prepared by vacuum depositions of metals on single crystal substrates in ultra-high vacuum (UHV) [1]. In this study, ORR activities are investigated for Pt/Co and Pt/Co-N model catalysts prepared on Pt(111) substrate by alternative arc-plasma depositions (APDs) of Pt and Co (Co-N).

The UHV-APD-EC apparatus is described elsewhere [2]. Pt and Co (Co-N) layers were alternately deposited onto a clean Pt(111) substrate by the APDs at 573K in UHV. As for the preparations of Co-N layers, Co was deposited by APD under 0.1 Pa of N2. Total thickness of the Pt/Co/Co-N and thickness of the topmost-surface Pt and bottom Co layers are fixed to be 6 nm, 1.6nm, and 0.4nm, respectively; the Pt(111)/Cox/Co(111) (denoted as U_Co_4A), U_Co_8A, U_Co_16A, and U_Co_32A samples are prepared. Structural analysis is performed by in-plane XRD, cross-sectional TEM. Then, the Pt/Co/Pt(111) and Pt/Co-N/Pt(111) samples were transferred to an N2-purged glove box without air exposure. Cyclic voltammetry (CV) and linearp sweep voltammetry (LSV) were performed without air exposure. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) showed that the CoOx(111) surface by sequentially adding another layer of Co-N layers.

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Catalyst for hydrogenation of CO. The main challenge in the development of Cu based transition - metal nanoparticles is thereby bring selectivity and efficiency to heterogeneous catalysis. Due to the wide range of accessible oxidation states (Cu(2), Cu(+) and Cu(3)), CuO-nanoparticles can promote and undergo a variety of reactions which enable reactivity via both one- and two-electron pathways. The size and shape of the particles can play an important role in reagent adsorption and activation at defects and dangling bonds.

In this study, we investigated the reaction mechanisms in carbon dioxide conversion with CuO nanoparticles synthesized through the photodeposition process on TiO2 nanoparticles supported on HOPG. We utilize ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to monitor the surface chemistry during in-situ catalytic reaction of CO2 and H2 (H2O) on the surface under ambient pressure conditions. To track the structural and morphological evolution of catalytic nanoparticles, SEM and TEM investigation will be reported.

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, as follows: The specific development of CuOx nanoparticles on TiO2 nanoparticles was supported through the Office of Science of the U.S. Department of Energy under Award No. DE-SC0004993; The ambient pressure XPS experiments were carried out at the CSX2 end station at NSLS-II. RG is supported by funding from the Provost Office of the University of California, Irvine.

5:00pm HCS+A+S-WeA-9 Atomic-Scale Characterization of Pt/Ag Surface Alloys, Dipna Patel, E Sykes, Tufts University

Catalytic hydrogenation reactions are important in many industrial applications. While Pt is catalytically active towards hydrogenation, it is very costly, can suffer from poisoning by CO and coke. On the other hand, bulk Ag is catalytically inert towards hydrogenation reactions, but cheaper than Pt and more resilient to poisoning. Previously, Ag based catalysts have been modified for applications in highly selective heterogeneous catalysis. By analogy to our single-atom alloy approach in other systems such as Pt/Cu and Pd/Cu, alloying Pt into Ag has the potential to greatly enhance catalytic selectivity while reducing the cost of precious metal required to catalyze industrially relevant reactions and reduce poisoning. The atomic-scale surface structure of dilute Pt-Ag alloys has not been reported to date. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of low coverage Pt deposited on Ag(111) as a function of temperature. At low temperatures, intermixing of Pt-Ag is driven by a negative mixing enthalpy, resulting in different metastable states such as isolated Pt atoms in, and islands on, Ag terraces, as well as Pt rich brims located along Ag step edges. Increasing the alloying temperature results in an increased concentration of Pt atoms along Ag step edges as well as direct exchange of Pt atoms into Ag terraces. At higher temperatures, there is sufficient thermal energy for Pt atoms to fully disperse in the Ag(111) surface layer as isolated atoms, forming single-atom alloys. This characterization of Pt-Ag surface alloys will enable us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and potentially tune catalytic selectivity and resilience to poisoning via both ligand and ensemble effects.

5:20pm HCS+A+S-WeA-10 Structural Consequences of High Oxygen Coverages on Rh(111), Rachael Farber12, M Turano, D Killelea, Loyola University Chicago

Partial oxidations of small molecules over metal surfaces are central to many heterogeneous catalyzed reactions. However, the identity of the actual surface species that promote or hinder these reactions has remained elusive for a variety of reasons. Recently, the understanding of the role of surface oxides in catalytic activity has changed. Instead of being thought of as poisons, they are now believed to be effective promoters of selective catalysis.

We have chosen to study oxidation on Rh(111) as a model system; Rh effectively promotes oxidation reactions and is a benchmark system for models of heterogeneously catalyzed chemistry. Our approach is to first elucidate the uptake of oxygen on Rh(111) and the surface structures formed for a range of oxygen coverages and then characterize them with a variety of techniques under ultra-high vacuum conditions. Exposure to O2 yields coverages up to 0.5 monolayers (ML), and higher coverages, well in excess of 1 ML, were achieved by dosing with gas-phase atomic oxygen (AO). The surface oxygen coverage was determined with Auger electron spectroscopy (AES), the total oxygen abundance with temperature programmed desorption (TPD), and the surface structures with low energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

Careful control of the exposure parameters allowed for the selective growth of the RhO2 surface oxide, surface adsorbed oxygen, and subsurface oxygen. The combination of AES, TPD, LEED, and STM revealed that despite total oxygen coverages in excess of 3 ML, the surface oxygen coverage was less than 1 ML and the thermodynamically favored surface phase was the (2x1)-O adlayer corresponding to a surface oxygen coverage of 0.5 ML. The RhO2 surface oxide was observed to form during extended oxygen exposures, but the (2x1) adlayer persisted. Our findings highlight the complexity of the surface chemistry of oxygen on transition metals and reveal the consequences of incorporating oxygen into the near-surface region of the solid. Furthermore, formation of the surface oxide was shown to rely not only on the presence of defects, but also on high concentrations of oxygen absorbed below the surface of the metal.

Small clusters exhibit electronic and chemical properties that can differ significantly from that of the bulk and offer a unique opportunity for preparing novel catalysts whose reactivity can be controlled at the atomic level. Here, we use mass-selected cluster deposition to prepare model “inverse” catalysts comprised of small metal oxide (M2O3: M = Ti, Nb, Mo, Ce, W) and sulfide (M2S3: M = Mo, W) clusters deposited on Cu, Cu2O/Cu and Au surfaces for studies the water-gas-shift reaction (WGS) and for CO/CO2 activation. A key advantage of cluster deposition is that it allows control over cluster stoichiometry which provides a means of introducing oxygen/sulfur “vacancies” and varying the average cation oxidation state. Recent work has focused on the correlation of electron transfer at the cluster-support interface and activity for water dissociation, the latter being a key step in the WGSR mechanism. Electron transfer is probed by XPS core level spectra and 2PPE photoemission measurements of coverage-dependent work function shifts to extract surface dipoles. All the oxide clusters on Cu(111) exhibit negative surface dipoles, indicative of Cu to cluster charge transfer, with smaller dips for sub-stoichiometric and reducible oxides (Ti, Nb). Temperature programmed reaction (TPR) experiments show that the Ti2O3 and Nb2O5 clusters promote water dissociation on Cu(111), with the “reduced” Ti2O3 clusters being more active, while both stoichiometric and reduced Nb2O5 clusters are active. Overall, these results suggest that local cation coordination is most important for determining water activity. Recent ambient pressure XPS (CO/H2O, 100’s mTorr) measurements at NSLS-II show that small Ti2O3 (n = 3, 4, 5) clusters on Cu(111) are active for the WGSR reaction through the observation of reaction-induced O-vacancy formation (Ti+ 2p) and the appearance of formate intermediates (C 1s) at room temperature. Results will also be presented on investigations of CO2 activation on alkali modified surfaces of Mo5S6 clusters on Au(111), which had been previously predicted to be active for CO2 hydrogenation to methanol. Combined TPR and XPS measurements show that co-deposition of K-atoms and Mo5S6 clusters strongly enhances CO2 adsorption above room temperature, whereas the CO2 is only weakly bound on the bare clusters. The results will be compared with DFT calculations of the possible CO2 binding sites for the K-cluster-Au interfaces.

This work was performed at Brookhaven National Laboratory under Contract No. DE-SC0012704 with the U.S DOE, Office of Science, and supported by its Division of Chemical Sciences, Geosciences, and Biosciences.
Novel Trends in Synchrotron and FEL-Based Analysis Focus
Topic
Room 9 - Session SA+AS+HC+SS-WeA
In Situ and Operando Characterization of Interfacial Reactions in Energy & Electronic Devices
Moderators: Karen Chen-Wiegart, Stony Brook University/Brookhaven National Laboratory, Elke Arenholz, Lawrence Berkeley National Laboratory
2:20pm SA+AS+HC+SS-WeA-1 Probing Solid-Gas and Solid-Liquid Interface Using APXPS, Zhi Liu, ShanghaiTech University, PR China; J Cai, Q Liu, ShanghaiTech University, PR China; Y Han, Chinese Academy of Sciences, PR China; J Liu, ShanghaiTech University, PR China; M Mao, H Zhang, Chinese Academy of Sciences, PR China; Y Li, ShanghaiTech University, PR China

INVITED
Multiple new ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations are currently under planning or development at US and international synchrotron light sources. Most of the research has been focused on the solid-gas interfaces. [1] Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV-5keV). By using X-ray up to 5keV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. [2] In this talk, I will present results of in-situ studies on the electrolyte/electrode interface of a working model electrochemical cell. I will also give a brief introduction on the APXPS development in Shanghai.

We believe the successful development of soft and hard X-ray APXPS techniques will provide us and community beyond a powerful in-situ tool to directly study interface phenomena at Solid-Gas and Solid-Liquid Interfaces.

References

3:00pm SA+AS+HC+SS-WeA-3 Graphene Capped Static and Fluidic Systems for In-Liquid Atmospheric Pressure XPS/AES/SEM and PEEM Studies of Electrochemical Interfaces, Hongxuan Guo, E Strelcov, A Yulaev, NIST, Center for Nanoscale Science and Technology; S Nemšák, D Mueller, C Schneider, Peter Grünberg Institute and Institute for Advanced Simulation, Germany; A Kolmakov, NIST, Center for Nanoscale Science and Technology.
The liquid-solid electrochemical interfaces are a central topic of modern energy-related electrochemistry and catalysis research. For the last two decades, this research line benefited greatly from the development of differentially pumped electron optics and refreshable sample delivery systems which became an experimental core of the modern ambient pressure electron spectroscopy. An alternative experimental approach to atmospheric pressure electron microscopy (SEM1, SPEM2, PEEM3) and spectroscopy (XPS4, XAS5) has been recently tested. In this approach, high electron transparency and molecular impermeability of the graphene membrane was employed to separate the liquid or gaseous sample from ultra-high vacuum environment of electron spectrometer.

In this presentation, we will show our recent work on design and performance of the static and fluidic microfabricated arrays (MCA) capped with bilayer graphene. With such a liquid cell, we characterized water and aqueous solution employing synchrotron-based and standard laboratory XPS, SEM, EDX, and Auger spectroscopy setups. In particular, Cu electroplating and copper sulfate electrolyte polarization at the graphene working electrode have been studied spectroscopically in real time and nanoscopic spatial resolution.

Acknowledgement
E5, HG, and AY acknowledge support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology, Award 70NANB14H209, through the University of Maryland.

Reference

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3:00pm SA+AS+HC+SS-WeA-3 Graphene Capped Static and Fluidic Systems for In-Liquid Atmospheric Pressure XPS/AES/SEM and PEEM Studies of Electrochemical Interfaces, Hongxuan Guo, E Strelcov, A Yulaev, NIST, Center for Nanoscale Science and Technology; S Nemšák, D Mueller, C Schneider, Peter Grünberg Institute and Institute for Advanced Simulation, Germany; A Kolmakov, NIST, Center for Nanoscale Science and Technology.
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Acknowledgement
E5, HG, and AY acknowledge support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology, Award 70NANB14H209, through the University of Maryland.

Reference


3:20pm SA+AS+HC+SS-WeA-7 In Operando Quantification of Valence Changes in Memristive Devices, R Dittmann, Christoph Baumer, Peter Grünberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany; D. Came, Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France; C. Schmitz, S Menzel, C Schneider, R Waser, Peter Grünberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany

INVITED
Memristive devices based on resistive switching in transition metal oxides are attractive candidates for next-generation non-volatile memory applications. It is suspected that voltage-driven oxygen-ion migration and the resulting nanoscale redox processes drive the resistance change in these materials1,2. Direct observation and quantification of the switching mechanism itself, however, remains challenging because the net changes of structure, stoichiometry, and valence state during switching are very small and occur primarily at electrode interfaces or within nanoscale filaments.

Here we will present local changes in the chemical and electronic structure of SrTiO3-based memristive devices utilizing in operando characterization tools like transmission electron microscopy (TEM) and photoemission electron microscopy (PEEM). SrTiO3 is chosen as a single crystalline model material, which offers a well-understood platform and well-characterized spectroscopic signatures.

To overcome the surface sensitivity typically limited PEEM investigations of resistive devices, photoelectron-transparent graphene top electrodes are used to attain spectroscopic information from the buried SrTiO3 layer3. During in situ switching, reversible changes of the O K-edge absorption spectra within spatially confined regions provide a quantitative map of the oxygen vacancy concentration, confirming that the resistance change is caused by localized oxygen evolution and reincorporation reactions rather than purely internal movement of oxygen vacancies4.

A remarkable agreement between experimental quantification of the redox state and device simulation reveals that changes in oxygen vacancy concentration by a factor of 2 at electrode-oxide interfaces cause a modulation of the effective Schottky barrier and lead to >2 orders of magnitude change in device resistance. These findings allow realistic device simulations, opening a route to less empirical and more predictive design of future memory cells.

1 R. Waser and M. Aono, Nat. Mater. 6, 833 (2007).
interface oxidation was enhanced. The enhanced interfacial oxidation rates were obtained from the differential of I_{O1s}. The P_{O2}(int) dependence of the interfacial oxidation rate shows that the O$_2$ pressure increase makes the interfacial oxidation rate fast, and the interface oxidation rate is proportional to the square root of P_{O2}(int).

This result cannot be explained using traditional oxidation models, because the proportional relationship between the interface oxidation rate and square root of P_{O2}(int) indicates that the interface oxidation rate is limited by an O$_2$ diffusion through the oxide. However, the thickness oxide is much thinner than 1 nm, so that it cannot be thought that the rate-limiting reaction of interfacial oxidation is O$_2$ diffusion. To explain the kinetics, we propose the new interference oxidation model named “Unified Si oxidation model mediated by point defects”[3].

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Applied Surface Science Division
Room 13 - Session AS+BI+SA+SS-ThM

Spectroscopy of the Changing Surface
Moderators: Timothy Nunney, Thermo Fisher Scientific, UK, Tony Ohlhausen, Sandia National Laboratory

8:00am AS+BI+SA+SS-ThM-1 In Situ Investigation of the Dynamic Transformations of Model Catalyst Surfaces using Ambient Pressure XPS, Iradjikhanari Walujo, Brookhaven National Laboratory

In heterogeneous catalysis, the interaction between reactant molecules and the surface of the catalyst often causes changes in the surface composition and chemical state of the catalyst, which may result in changes in the reactivity of the catalyst. Using ambient pressure x-ray photoelectron spectroscopy (AP-XPS), these changes can be monitored in situ under close-to-realistic conditions. Unlike conventional XPS, which requires UHV conditions, AP-XPS measurements can be performed in the presence of gases at pressures of up to 100 Torr through the use of differentially pumped analyzer, small analyzer entrance aperture, and x-ray transparent windows. Although AP-XPS measurements using lab x-ray sources are possible and becoming more common, experiments at modern synchrotron light sources have distinct and significant advantages including tunable photon energy, tightly focused beam, and better resolution. A general overview of the technique as well as recent experimental results will be presented. Examples shown include (1) the potassium-promoted reduction of CuO/Cu(111) by CO, in which the reduction of Cu to Cu(0) is accelerated by the presence of K through the formation of surface carbonate species, (2) the surface segregation of Pt/Cu(111) model bimetallic catalyst in the presence of various reactant gases, and (3) the reduction of CuO/Pt/Cu(111) by H2.

8:40am AS+BI+SA+SS-ThM-3 Observation of Oxygen Binding on PGM-free Electrocatalysts by Ambient Pressure XPS and XAS, Kateryna Art'yushkova, University of New Mexico; M Dzara, S Pylypenko, Colorado School of Mines; P Atanassov, University of New Mexico

The most promising class of PGM-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). They show promise as replacement of Pt in two different technological platforms - alkaline exchange membrane fuel cells (AEMFCs) and proton exchange membrane fuel cells (PEMFCs). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the exact nature of the active sites is still debated even after over 50 years of research. Understanding the specific roles of nitrogen and metal in the properties/activity/stability/durability of MNC-based catalytic materials is a prerequisite for the rational design of ORR electrocatalysts with improved performance.

The key component in elucidating the relationship between the chemistry of active sites and activity is a better understanding of the formation of adsorbates, intermediates, and products during reactions occurring within the fuel cell. In situ monitoring reaction steps under realistic conditions in metal-free and metal-containing building blocks will shed light onto the reaction mechanism that is essential for developing active and durable PGM-free catalyst for ORR.

We will report on AP-XPS analysis for series of electrocatalysts belonging to Fe-N-carbon families based on sacrificial support method (SSM) and Metal-organic frameworks (MOF). The effect the nitrogen chemistry and the type of iron have on the oxygen binding was investigated by ambient pressure X-ray Photoelectron Spectroscopy (XPS) and X-ray Adsorption Spectroscopy (XAS) under an O2 environment at operating temperature of the fuel cell. The effect of the relative abundance of different types of nitrogen, such as pyridinic, coordinated to iron and hydrogenated nitrogens (pyrolic and hydrogenated pyridine) on the preference of oxygen binding is studied by high-resolution nitrogen photoelectron spectra. The role of metallic and atomically dispersed iron will be investigated by a combination of XAS and XPS. Linking differences in oxygen binding to the differences in the chemistry of the electrocatalysts is of ultimate importance for elucidating the oxygen reduction reaction mechanism.


9:00am AS+BI+SA+SS-ThM-4 In situ Monitoring of Electrochemically Generated Carbene by XPS, Pinar Aydogan Gokturk1, S Donmez, Y Turkm en, B Uğur, S Suzer, Bilkent University, Turkey

Ionic liquids provide a platform for fundamental electrochemical studies in vacuum. In this present work, we report an in-situ X-ray photoelectron spectroscopic (XPS) investigation of N-heterocyclic carbene(NHC) generation from the electrochemical reduction of imidazolium based ionic liquids (ILs) through changes in oxidation state of nitrogen atoms. The IL serves as an electroactive material as well as the electrolyte in the cell between a Si substrate which is connected to the instrument ground and a gold wire connected to the sample holder for electrical connection. Through the course of the electrochemical reaction, the positive charge on imidazolium cation is neutralized to give free NHC as reflected by the distinct shifts in the N 1s and C 1s binding energies. The observations are further supported by colorful adduct formation of carbenes with Cs2, reversible redox peaks in the voltamogram and the density functional theory calculations. The presented structure and XPS measurements can lead on understanding of the mechanism for various electrochemical reactions.

9:20am AS+BI+SA+SS-ThM-5 The Influence of Water on the Ionic Liquid-Vapor Interface, John Newberg, University of Delaware; M Shiflett, University of Kansas; A Broderick, Y Khalifa, University of Delaware

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions and it is important we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction and electrochemical window. In this talk we will highlight our recent efforts examining the IL-water interface utilizing ambient pressure X-ray photoelectron spectroscopy (APXPS). APXPS allows for a molecular level assessment of the IL-vapor interface including a quantitative assessment of interfacial water concentration, moiety specific electronic environment changes, structural changes and obtaining adsorbate energetics.

9:40am AS+BI+SA+SS-ThM-6 Ambient Pressure XPS Studies of Model N-C and Fe-N-C Catalysts Under Oxygen Environment, Michael Dzara, Colorado School of Mines; K Art'yushkova, University of New Mexico; C Nga, M Strand, J Hagen, S Pylypenko, Colorado School of Mines

Producing inexpensive polymer electrolyte membrane fuel cells requires significant reduction in the amount of platinum group metal (PGM) oxygen reduction reaction (ORR) catalyst used. High surface area iron- and nitrogen-functionalized carbon (Fe-N-C) materials are a promising PGM-free replacement. These catalysts are very heterogeneous, leading to difficulties in discerning contributions from various potential active sites and identifying the most active species.1 Techniques such as scanning transmission electron microscopy (STEM), energy dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) provide structural and chemical information that can be correlated to ORR activity measured with electrochemical methods. Ambient pressure XPS (AP-XPS) and x-ray absorption spectroscopy (XAS) conducted in a humidified O2 environment, at an elevated temperature, and with applied potential offer opportunities to study materials under in situ conditions to determine adsorbates, intermediates, and products during ORR steps.2,3

In this work, model Fe-N-C catalysts are studied along with reference nitrogen-doped carbon (N-C) materials. Development of model catalyst materials with controlled morphology and speciation can simplify the elucidation of active sites. Micro-porous N-C nanospheres with high graphic content were synthesized by a solvothermal treatment of resorcilon, formaldehyde, and ethylenediamine, and a subsequent pyrolysis in N2.4 Incorporation of Fe into the N-C nanospheres was carried out by wet-impregnation of various Fe precursors followed by a second N2 pyrolysis. By varying synthetic parameters, a set of N-C and Fe-N-C nanospheres with diverse intertextural positions and properties were produced. Differences in composition and structural were evaluated using STEM-EDS and XPS, demonstrating control over N and Fe quantity and speciation. Select N-C and Fe-N-C nanospheres were then characterized with in situ AP-XPS, and in the case of Fe-N-C nanospheres, in situ XAS. By understanding the ORR on these model Fe-N-C nanospheres, synthesis-property-performance conclusions are drawn, guiding the development of highly active Fe-N-C catalysts.

1 ASSD Student Award Finalist
The samples for oxidation were p-Si(001) and n-Si(001) surfaces. The dopants were Boron and arsenic for p- and n-type substrates, respectively. Their density of dopants were approximately $10^{20}$ atoms/cm$^2$ so extrinsic region can be kept in the high temperature region even below 700°C. These samples were oxidized using $O_2$ gas at the pressure of $1.0 \times 10^5$ Pa. During the oxidation reaction, the photoelectron spectra were measured repeatedly, therefore time evolution of the amount of oxygen adsorption, work function, and band bending can be investigated.

In the room temperature oxidation, it is found that oxidation reaction coefficient on n-Si(001) is larger than that on p-Si(001). To clarify the reasons, we focus to the change of work function due to the formation of dipole layer. The work function of the n-Si(001) surface shows negative value but p-Si(001) is positive value. From this result, we can estimate the adsorption positions of O atoms. O atoms have a negative charge in the bond of Si-O, so it can be assumed that oxygen is placed on the n-Si(001) surfaces, but it is subsurface in case of the p-Si(001) surface. In case of n-Si(001) substrates, the doped electrons spill out into the surface because many electrons exist in the substrate. As the result, oxidation reaction is promoted in the n-Si(001) surface. From these results, we found that there is a difference of oxidation kinetics depending on the conductivity. In the presentation, we will also show a difference of oxide states between them.

Biomaterial Interfaces Division
Room 12 - Session B+AS+SA-ThM

Characterisation of Biological and Biomaterial Surfaces
Moderators: Daniel Graham, University of Washington, Tobias Weidner, Aarhus University, Denmark

8:00am B+AS+SA-ThM-1 Lipid Involvement in the Regenerative Processes of Dugesia dorotocephala - A GCB ToF-SIMS Imaging Study, Tina Angerrger, M Taylor, D Graham, L Gamble, University of Washington

Dugesia dorotocephala are planaria belonging to the class of Turbellaria, or non-parasitic flat worms. They are best known for their fascinating regenerative abilities, which allow them to be cut into more than 200 pieces, each piece missing essential parts necessary for the worms’ survival and each regenerating a new individual. This level of reorganization involves a complex interplay of a wide range of molecules that varies spatially and temporally but is still poorly understood.

Recently the involvement of peptides and proteins in the process of regrowing the head and developing a new central nervous system has been studied by Sweedler et al using MALDI imaging. MALDI, in contrast to TOF-SIMS imaging, is capable of studying the distributions of peptides in tissue but spatial resolution is limited and molecules of interest have to be partially predetermined by the choice of matrix.
Lipids are a diverse group of molecules fulfilling numerous functions such as energy storage and cell signaling, however lipid and fatty acid data for Dugesia in general is very limited and their localizations completely unknown. Our studies were targeted at establishing a full body lipid profile for the different organ systems present in Dugesia as well as monitoring their changes due to stem cell migration during head regrowth and eye/CNS regeneration.

Dugesia flatworms were sectioned on a cryomicrotome at -20 °C and slices were placed on ITO coated glass. After preparation samples were immediately taken to the lab for analysis. Sample preparation and transport time was kept to less than 2 hours to minimize lipid degradation. After SIMS analysis, optical images were acquired in order to facilitate identification of structures seen within the worms. To deal with the increased spectral and spatial complexity provided by our improved instrumental capabilities, imaging PCA was used to "untangle" the data. In this presentation we will present the results of our studies showing the unique lipid distributions throughout Dugesia cross sections and discuss their relevance.


9:20am Bi+AS+SA-ThM-2 Can ToF-SIMS Imaging Explain Biology?, Lara Gamble, D Graham, University of Washington

Imaging time-of-flight mass spectrometry (ToF-SIMS) can provide images of cells and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as the role of changes in tumor metabolism affecting the response to chemotherapy is under scrutiny. Regions of interest (ROIs) of the tumor can be utilized to compare similar regions from different tissue samples. PCA analysis of ToF-SIMS image data reveals the differences in chemistries between the regions. These results help to identify links between the chemical composition within and around tumors and the changes of these tumors as a response to the treatment. However, often the presentation of ToF-SIMS results might not be in the best format to gain the interest of non-SIMS scientists. Different data processing and data presentation format from clinical trial tissue samples and other tissue samples analyzed with ToF-SIMS will be presented. Additional validation of data interpretation from different techniques will be discussed.

9:40am Bi+AS+SA-ThM-3 Applications of XPS for Novel Biomaterial Systems, Jonathan Counsell, S Couttas, C Blomfield, Kratos Analytical Limited, UK; C Moffitt, Kratos Analytical; S Hutton, Kratos Analytical Limited, UK, United Kingdom of Great Britain and Northern Ireland

INVITED XPS is widely used in the field of biomaterials yielding quantitative elemental and chemical state information. It is possible to identify changes in functional groups present both on the surface and, combined with depth profiling, within the bulk of a biomaterial. Here we will discuss the latest advancements in XPS as applied to a range of biomaterial systems and examine new possibilities beyond routine spectroscopic analysis. Non-destructive depth profiling of the near surface region is applied to ultra-thin films examining growth modes and film closure mechanisms. With the dual Al/Ag monochromated sources it is possible to vary information depth for relative comparisons on the nature of the uppermost layers. New developments in cluster ion sources now allow soft biomaterials to be depth profiled. Accurate analysis of interfacial chemistry is possible without ion beam damage. XP imaging will also be discussed for systems exhibiting surface inhomogeneity. Quantitative images yield useful additional information over conventional microscopies. Discussions will concentrate on both model systems and real life applications highlighting the latest possibilities of XPS for this growing field.

As next step the vertical adhesion forces of a single bacterium were measured as a function of pH, ionic strength, and substrate. The adhesion force of one single cell decreases from pH 4 to pH 9. As a function of the ionic strength, the adhesion forces increase with increasing salt concentration with a pronounced spike (higher adhesion forces) at 0.9 % NaCl. All adhesion force changes completely correlate with the electrostatics as determined by zetapotential measurements. A conditioning film of growth medium strongly decreases the adhesion forces. Thus the first bacterial layer should grow without medium at pH 4.

In a last step, the lateral detachment forces of the bacteria were measured. There is a clear correlation between the applied force and the number of moved bacteria, but the detachment forces vary for the individual bacteria. For small lateral forces (0.5 nN), the wettability of the substrate seems to control the detachment process. For higher lateral forces (2-3 nN), the effect of the wettability gets lost and the roughness of the samples controls the cell detachment. These detachment forces are in the same range or higher than the shear forces applied by the fluid flow.

11:00am BI+AS+SA-THM-10 AVS 2017 Peter Mark Memorial Award Lecture: A Combined Experimental–Simulation Approach for Unraveling Hydrophobic Interactions at the Molecular Scale, P Stock, MPI for Iron Research, Germany; J Monroe, UC Santa Barbara; T Utzig, MPI for Iron Research, Germany; D Smith, S Shell, UC Santa Barbara; Markus Valtinier1, TU Bergakademie Freiberg, Germany INVITED Interactions between hydrophobic moieties steer ubiquitous processes in aqueous media, including the self-organization of biologic matter. Recent decades have seen tremendous progress in understanding these for macroscopic hydrophobic interfaces. Yet, it is still a challenge to experimentally measure hydrophobic interactions (HIs) at the single-molecule scale and thus to compare with theory. Here, I will present a combined experimental–simulation approach to directly measure and quantify the sequence dependence and additivity of Hs in peptide systems at the single-molecule scale. We combined dynamic single-molecule force spectroscopy on model peptides with fully atomistic, both equilibrium and nonequilibrium, molecular dynamics (MD) simulations of the same systems. Specifically, we mutate a flexible (GS) peptide scaffold with increasing numbers of hydrophobic leucine monomers and measure the peptides’ desorption from hydrophobic self-assembled monolayer surfaces. Based on the analysis of nonequilibrium work-trajectories, we measure an interaction free energy that scales linearly with 3.0–3.4 kT per leucine. In good agreement, simulations indicate a similar trend with 2.1 kT per leucine, while also providing a detailed molecular view into Hs. Our approach potentially provides a roadmap for directly extracting qualitative and quantitative single-molecule interactions at solid/liquid interfaces in a wide range of fields, including interactions at biointerfaces and adhesive interactions in industrial applications. In this context, I will finally discuss in detail how single molecule unbending energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to adhesive failure under corrosive and wet conditions.

1 S. Raman et al. in Nature Communications, 5(2014), 5539.

11:40am BI+AS+SA-THM-12 Quantitative Characterization of Bacterial Cells in Solution and on Surfaces, C Sousa, K Jankowska, I Parga Basanta, I Pinto, Dmitri Petrovykh, International Iberian Nanotechnology Laboratory, Portugal Physicochemical properties of bacterial cells make them challenging subjects for methods typically used to characterize micro- and nanoparticles. Even for conceptually simple parameters, such as size and concentration, direct characterization of live bacteria (and their agglomerates) in solution is far from trivial because bacterial cells are soft and often anisotropic particles with sizes of not more than a few microns. Low contrast, in terms of optical and electronic properties, between bacteria and their aqueous environment complicates any attempted direct measurements in solution. Comparing bacterial cells to non-biological micro- or nanoparticles, whether in the context of mixed samples or calibration measurements, further compounds the complexity of characterizing these systems.

We are using Staphyloccocus aureus (S. aureus) bacteria as a model system for quantitative characterization of bacterial cells. For systematic measurements, S. aureus bacteria offer the advantages of nearly spherical shape and of robust viability under a wide range of experimental conditions and treatments. The approximately one micron diameter of live S. aureus cells also makes them representative of the sensitivity and resolution challenges encountered in the characterization of bacterial cells. In microscopy, for example, the size of individual bacterial cells changes dramatically as they are prepared for measurements with increased spatial resolution: from confocal optical microscopy, to environmental scanning electron microscopy (SEM), to TEM in vacuum. The objective of our work is to develop and validate a set of complementary techniques that can be used to characterize live bacterial cells. We will describe the use of nanoporous membranes with S. aureus suspensions and commonly overlooked effects of centrifugation, mechanical agitation, and other typical sample preparation procedures on the apparent distribution and properties of particles in biological samples. The forced contact of bacteria with these membranes during filtering also suggests their use as model systems for investigating the interactions of bacteria with surfaces having different chemistries and/or morphological features.

12:00pm BI+AS+SA-THM-13 In Situ Multimodal Imaging of Microbial Communities, Xiao-Ying Yu, Pacific Northwest National Laboratory We developed a vacuum compatible microfluidic interface, System for Analysis of the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a variety of spectroscopy and microscopy characterization techniques. SALVI was recently applied to investigate biological interfaces in living biofilms and co-cultured microbial communities. In this talk, two case studies will be presented using in situ liquid ToF-SIMS, light microscopy, and fluorescence microscopy. In the first case study, Shewanella wild type and mutant were both exposed to environmental stressors such as toxic heavy metal ions (i.e., Cr (VI)) and silver nanoparticles. The response of biofilm and its extracellular polymeric substance (EPS) to the environmental perturbation was investigated using in situ liquid SIMS coupled with structured illumination microscopy (SIM). In the second case, a more complex microbial communities consisting of syntrophic Geobacter metallireductor and Geobacter sulfurreducens was investigated. Electron donor and electron acceptor in this co-cultured microbial system were characterized first using the more traditional SIMS dry biological sample preparation approach followed by in situ liquid SIMS and confocal laser scanning microscopy (CLSM). The electron transfer between the two species was probed dynamically using the electrochemical SALVI. Correlative imaging is employed to achieve a more holistic view of complexed microbial systems across different space scales. Our results demonstrate that interfacial chemistry involving living microbial systems can be studied from the bottom up based on microfluidics, potentially providing more important understanding in system biology.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic Room 24 - Session HC+SA+SS-THM Mechanisms and Reaction Pathways in Heterogeneously Catalyzed Reactions Moderator: David Payne, Imperial College London 8:00am HC+SA+SS-THM-1 Effects of Phosphorus and Alkyl Substituents on C-H, C-C, and C-O Bond Rupture within Carboxylic Acids on Ru(0001), SIWei A. Chang, D Floherty, University of Illinois at Urbana-Champaign Transition metal phosphide (TMP) catalysts are selective towards C-O bond rupture during hydrodeoxygenation reactions used to upgrade bio-oil. However, the manner in which bond rupture mechanisms and intrinsic barriers (i.e., C-H, C-C, and C-O bond) differ between transition metals and TMP catalysts are not well understood. In this study, a phosphorus (P) modified Ru(0001) surface is created using sequences of P2H adsorption and annealing treatments followed by Auger electron spectroscopy to determine the P:Ru ratio. Synthesized P0.5:Ru(0001) surfaces have a (7x7) low energy electron diffraction pattern and appear to resemble the (111) facet of bulk RuP materials. The results from temperature programmed desorption of CO and NH3 demonstrate that the addition of P atoms to Ru(0001) decreases the binding energy of CO and NH3 by ∼12 kJ mol⁻¹.

1 Peter Mark Memorial Award Winner

Thursday Morning, November 2, 2017

32

8:00 AM

Saturday, November 4, 2017
compared to Ru, suggesting that P atoms decrease the extent of electron exchange between Ru surfaces and adsorbates (i.e., CO and NH_3). Results from temperature programmed reaction (TPR) of C_4-C_9 carboxylic acid decomposition on Ru(0001) and P_2-xRu(0001) surfaces indicate that both P atoms and the length of alkyl substituents on carboxylic acids (i.e., R = H, CH_3, CH_2CH_3, and CH_3CH_2CH_3) alter the intrinsic activation energy (E_a) of bond ruptures. On both surfaces, TPR and reactive molecular beam scattering (RMBSS) results are consistent with carboxylic acid decomposition mechanism, that involves the reaction of carboxylate intermediates to form alkyl surface species with either CO (by C-O bond rupture followed by C-H/C-C bond rupture) or CO_2 (by direct C-H/C-C bond rupture). The addition of P atoms to Ru(0001) increases E_a values for the rupture of all bonds (i.e., C=O, C-H and C-C bonds) by 5-50 kJ mol^{-1} and increases also the ratio of CO to CO_2 production (in the case of formic acid and acetic acid decomposition). In addition, P atoms weaken the linear correlation that exists between E_a for C=C and C-H bond rupture and the homolytic bond dissociation energies (BDE) of the involved bonds (e.g., R-COOH), thereby decreasing the strength of the correlation from near parity on Ru(0001) (i.e., slope m = 1) to moderate changes with BDE on P_2-xRu(0001) (i.e., slope m = 0.2). The RMBSS results from formic acid in the presence of P atoms show a higher production of CO than CO_2, which reflects the catalytic consequences of the differences between the C-H and C-O bond rupture energy barriers on P_2-xRu(0001) and those for Ru(0001). Collectively, these results suggest that P atoms alter the production selectivity of CO and CO_2 through a greater energy in the energy barriers of C-O bond relative to C-H/C-C bond rupture.

8:20am **HC+SA++SS-ThM-2 Monitoring Cu(111) Restructuring under Elevated CO Pressures via Polarization Dependent Infrared Spectroscopy, Christopher Kruppe, M Trenary, University of Illinois at Chicago**

Recently it was shown that a Cu(111) surface will reconstruct to form nanoclusters when exposed to 0.1 – 100 Torr of CO. We present the use of polarization dependent – reflection absorption infrared spectroscopy (PD-RAIRS) to monitor the Cu(111) restructuring in real time. Under 10 Torr of CO, PD-RAIR spectra display a peak for CO on top of Cu atoms. Scans were taken periodically and displayed new peaks related to CO bond to the nanoclusters that grow over a period of 30 minutes. Spectra obtained at 10 Torr and 300 K show that the creation of the Cu nanoclusters is correlated with an increase in intensity of these C-O vibrational features, which are only visible due to removal of gas phase CO features from the RAIR spectra. Dissociation of H_2O in UHV occurs on the nanoclusters, which is negligible on unreconstructed Cu(111). Previously the splitting of H_2O was thought to be a geometric effect caused by the nanocluster surface that is not adsorb on Cu(111) at room temperature. However, after exposing Cu(111) to 10 Torr of CO at room temperature for 30 minutes strong C-O vibrations are observed upon evacuation of the IR cell. In UHV, the H_2O partial pressure is increased in the IR cell to 2 × 10^5 Torr and flowed over the reconstructed Cu(111) crystal. The RAIR spectra indicates that there is another reaction that occurs with H_2O to create formaldehyde. This is further confirmed by observing formaldehyde with temperature programmed desorption following H_2O exposure. Auger electron spectroscopy confirms the presence of oxygen on the Cu(111) surface after water exposures in the IR cell. Detailed interpretation of the data requires consideration for the formation of Fe-carboxyl, which can be present in the CO bottle, or produced in the reaction cell. The possibility of Fe as the cause for the CO bond in UHV will be presented.


The simplest reaction studied in the plasma reactor is the dissociation of CO: into CO and O. We find energy efficiencies higher than 45%, indicating that the system is not in thermodynamic equilibrium and plasma favors vibrational excitation to translational heating. Adding a catalyst like AgO or NIO on Al_2O_3 does not enhance the yield. However, a purely metallic catalyst does significantly enhance the yield.

Optical emission spectroscopy shows that the radiofrequency (RF) and microwave (MW) plasma behave quite different. In the MW plasma predominantly emission from the C_2 Swan-band is seen, whereas the RF plasma shows mainly chemiluminescence from excited CO. This is due to a different electron excitation mechanism.

In the case of dry reforming of CH_4 with CO: in the plasma reactor we find that addition of an oxidizing catalyst does not enhance the yield of CO + H_2. In the case of dry reforming of butane (C_4H_10) to yield butene (C_4H_8), plasma reforming with or without catalyst does shows only small conversion. Mainly cracking of butane into C_4H_4 is seen and polymerization. However, running the same reaction under high temperature conditions in a thermal reactor yields a satisfactory conversion. A Co based catalyst has the best performance.

These studies allow us to obtain mechanistic information on the conversion of simple molecules, pretreated by plasma, on various catalysts. We are exploring to what extend direct Eley-Rideal reactions are relevant in the plasma reactor. This reaction mechanism is very unlikely under thermal conditions.

9:20am **HC+SA++SS-ThM-5 Imaging the Molecular Origins of Symmetry Breaking on Well-defined Surfaces, Amanda Larson, R Hannagan, E Sykes, Tufts University**

Understanding the interaction of prochiral reactants with chiral modifiers on surfaces is a key step towards controlling heterogeneous enantioselective catalysis. We have chosen a simple model system composed of interacting chiral propylene oxide and propene molecules on a Cu(111) surface that is amenable to both scanning probe and desorption studies. Low temperature scanning tunneling microscopy (STM) enables an unprecedented level of spatial resolution of the enantioselective molecule-molecule interactions and their dynamics. STM imaging of propylene oxide and propene molecules at 5 K reveals that both molecules, when in isolation on the surface, behave as molecular rotors. Furthermore, the chirality of individual propylene oxide molecules can be discerned from the STM images of the rotating molecule. While propene is achiral in the gas phase it become chiral when bound to surfaces and STM also allows us to distinguish between its surface-bound enantiomers. When studied separately, repulsive forces between both sets of molecules disperse them on the surface at low coverages. However, when co-dosed we observe an attraction between propylene oxide and propene and they form complexes in which their rotation is inhibited. Temperature programmed desorption measurements are used to quantify these chiral modifier-molecule interaction strengths. Finally, the geometry of individual propene and propylene oxide molecules can be determined within the complexities and 1:1 chiral interactions deciphered.

11:00am **HC+SA++SS-ThM-10 A Surface Science Approach for New Heterogeneous Catalyst, Ib Chorkendorff, Technical University of Denmark, Denmark**

**INVITED**

First, we shall discuss how surface science and mass-selected nanoparticles can be used to make efficient model systems for heterogeneous catalysts. We shall demonstrate how mass-selected nanoparticles of CuZn alloys can be used to elucidate the dynamics of the methanol synthesis catalysts. The produced nanoparticles will be compared to the conventional CuZnAl at 1 bar for synthesizing methanol from CO_2 and H_2 [1, 2, 3]. The methanol synthesis on CuZn will also be discussed with respect to our recent findings of using alloys of NiGa for methanol synthesis [4]. The use of mass-selected nanoparticles will be further demonstrated for electrochemical Oxygen

**Thursday Morning, November 2, 2017**

**8:00 AM**
Reduction Reaction, which is really the limiting reaction in Proton Exchange Membrane Fuel Cells. Here we have found entirely new classes of electrocatalysts by alloying Pt with early transition metals [5] or the lanthanides [6]. We have also shown that it is possible to make mass-selected nanoparticles of these alloys with very good activities [7] and PtGd alloys [8]. Finally, we shall also discuss how planar surface science can be used to identify new catalysts for ammonia oxidation. We shall demonstrate how Copper deposited on Ruthenium can enhance the activity substantially and give rational explanations for this enhancement which also can be transferred to high area catalysts used for diesel exhaust treatment [9].

References

11:40am HC+SA+SS-ThM-12 Chemisorption and Oxidation of H2 on IrOx(110). Tao Li, Z Liang, University of Florida, Gainesville; M Kim, A Asthagiri, The Ohio State University; J Weaver, University of Florida, Gainesville

Understanding the interactions of hydrogen with IrOx surfaces is central to improving applications of electrocatalysis as well as exploiting the high-reactivity of IrOx for promoting methane activation. In this talk, I will discuss our recent investigations of the dissociative chemisorption and oxidation of H2 on stoichiometric and oxygen-rich IrOx(110) surfaces. We find that H2 dissociation is highly facile on s-IrOx(110), with more than 90% of a saturated H2 layer dissociating below 225 K during temperature-programmed reaction spectroscopy (TPRS). We observe only H2O desorption in a broad TPRS peak from about 400 to 780 K after generating low H2 coverages on s-IrOx(110) at about 90 K. At high H2 coverages, we also observe small H2 desorption peaks at 200 and 530 K which we attribute to molecular and recombinitive desorption processes, respectively. We present evidence that H2 dissociation on IrOx(110) occurs through a mechanism wherein H2-o complexes adsorbed on the coordinatively-unsaturated (cus) Ir atoms serve as precursors for H2 dissociation. We show that oxygen adsorbed on the cus Ir sites, so-called on-top O-atoms, hinder H2 dissociation on IrOx(110), while also facilitating H2O desorption and promoting H-atom transfer from bridging O-atoms to on-top O-atoms. I will also discuss the results of density functional theory calculations of H2 dissociation and initial steps of H2 oxidation on stoichiometric and O-rich IrOx(110).

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 9 - Session SA+AC+MI-ThM

Frontiers in Probing Properties and Dynamics of Nanostructures and Correlation Spectroscopy
Moderators: Jan Vogel, Institut Néel, CNRS/UGA, Grenoble, France; Christian Gutt, University of Siegen, Germany

8:00am SA+AC+MI-ThM-1 X-rays Revealing Exotic Properties of Magnetoelectric Multiferroics and Related Materials, Elke Arenholz, Lawrence Berkeley National Laboratory

Engineering novel materials with structural, electronic and/or magnetic characteristics beyond what is found in bulk systems is possible today through the technique of thin film epitaxy, effectively a method of ‘spray painting’ atoms on single crystalline substrates to create precisely customized thin films or layered structures with atomic arrangements defined by the underlying substrate. The abrupt change of composition as well as charge and spin transfer across interfaces can also lead to intriguing and important new phenomena testing our understanding of basic physics and creating new functionalities.

We use soft x-ray spectroscopy and scattering to probe and understand the electronic, magnetic and structural characteristics of novel engineered materials such as magnetoelectric multiferroics, i.e. materials that exhibit simultaneous order in their electric and magnetic ground states. These materials hold promise for use in next-generation memory devices in which electric fields control magnetism but are exceedingly rare in bulk form. Engineering magnetoelectric multiferroics by interleaving two or more atomically thin layers is an intriguing new approach. A very recent example is establishing room temperature coexisting ferromagnetic and ferroelectric order in LuFeO3/LuFe2O4 superlattices. [1] We used soft x-ray spectroscopy and microscopy to characterize the magnetic order and ferroelectric polarization of the system.

Similarly intriguing is engineering the orbital symmetry of emergent quantum states near the Fermi edge at interfaces determining the mobility of interfacial conduction electrons in novel heterostructures. Using soft x-ray linear dichroism (XLD), we investigated the orbital states of interfacial electrons in Al2O3/SrTiO3 and developed an interesting route to engineer emergent quantum states with deterministic orbital symmetry [2].


8:40am SA+AC+MI-ThM-3 X-ray Reflectivity Investigations of Ultrafast Dynamics in Magnetic Multilayer Structures, Christian Gutt, T Sant, D Ksenzov, U Pietsch, University of Siegen, Germany; J Luening, Sorbonne University; F Capotondi, E Pedersoli, M Manfreda, M Kiskinova, Elettra-Sincrotrone Trieste, Italy; M Klepae, H Zabel, University of Mainz

INVITED

Exciting a ferromagnetic material with an ultrashort IR laser pulse is known to induce a reduction of magnetic order and ultrafast spin diffusion processes. Both processes produce disorder on 100 fs scales and their role in a deterministic creation and switching of magnetic order is still poorly understood. Here, we demonstrate that a nanoscale magnetization-reversal exists in the vicinity of domain walls in the near-surface region of a ferromagnetic Co/Pd thin film upon IR excitation. This magnetization-reversal is driven by the different transport properties of majority and minority carriers through a magnetically disordered domain network we followed the ultrafast temporal evolution by means of an ultrafast resonant magnetic scattering experiment in surface scattering geometry, which enables to exploit the domain network within the top 3 nm to 5 nm layers of the FM film. We observed magnetization-reversal close to the domain wall boundaries that becomes more pronounced moving closer to the film surface. Its lateral extension has allowed us to measure the ultrafast spin-diffusion coefficients and ultrafast spin velocities for majority and minority carriers upon IR excitation.

9:20am SA+AC+MI-ThM-5 Spray Deposition of Water-processed Active Layers of Hybrid Solar Cells investigated with In situ X-ray Scattering Methods, Volker Körstgens, F Buschek, M Wörle, Technische Universität München, Germany; W Ohm, DESY, Germany; H Igles, Technische Universität München, Germany; S Roth, DESY, Germany; R Kienberger, P Müller-Buschbaum, Technische Universität München, Germany

In the development of non-conventional solar cells not only the achievements of highest power conversion efficiencies and maximum lifetime of devices is of interest. Also the sustainability of the production process of the devices comes into focus. In order to achieve an all-embracing green technology, the materials applied and the required energy for device fabrication are of importance. Materials in terms of functional components or as additives in the processing should be non-toxic and environmentally friendly. In an optimum approach no organic solvents could be used for the coating of any of the layers of the corresponding devices. High temperature processing steps should be reduced or avoided to increase the energy payback times of the solar cells. Following this idea, we developed hybrid solar cells with an active layer based on low temperature processed titania and a water-soluble polymer [1]. In our approach titania nanoparticles are produced with laser ablation in liquid in order to initiate a functionalization of titania with the polymer for the active layer. Combining these titania nanoparticles and water-soluble poly[3-(potassium-6-hexanoate)phenoxy-2,5-diyl] (P3P6T) hybrid solar cells are realized. In order to improve conversion efficiencies of these devices a vertical compositional gradient of the two components of the active layer was introduced. For the fabrication of hybrid photovoltaic devices we applied spray-coating as the deposition method for the active layer which could easily scale-up to industrial cost-effective fabrication. For the deposition of the active layer with laser-ablated particles spray
deposition provides a good control of the film thickness. The morphology of the active layer is of major importance for the performance of hybrid solar cells. We are especially interested in how the morphology changes with ongoing deposition process. Therefore we followed the development of the morphology of the active layer in situ with high spatial and temporal resolution. The mesoscale was probed with in situ GISAXS, whereas the crystallinity of the polymer and the inorganic component was investigated with in situ GIWAXS. The changes of the morphology and the influence on photovoltaic performance with the introduction of a compositional gradient are discussed. As the synchrotron-based investigation allowed for a high temporal resolution of 0.1 s, insights into the very first stages of the deposition process were obtained. From the overall situ study improvements for the spray deposition procedure are derived that allow for a better control of the morphology of the devices.


9:40am **SA+AC+MI-ThM-6 New Instrumentation for Spin-integrated and Spin-resolved Momentum Microscopy – METIS and KREIOS, Thomas Schultmeyer, M Wietstruk, A Thissen, SPECS Surface Nano Analysis GmbH, Germany; G Schoenhense, Johannes Gutenberg-Universität, Germany; A Oelsner, Surface Concept GmbH, Germany; C Tusche, Max Planck Institute for Microstructure Physics, Germany**

Two new momentum microscopes are presented by SPECS: our newly developed time-of-flight momentum microscope METIS and the energy dispersive and filtered momentum microscope KREIOS. Both are using an optimized lens design which provides simultaneously highest energy, angular and lateral resolution. The lens provides a full 2π solid acceptance angle with highest angular resolution, in contrast to standard ARPES measurements with conventional hemispherical analyzers, electronic structure data from and beyond the 1st Brillouin zone is recorded without any sample movement. In addition the lens of such an instrument can work in a lateral imaging mode for microscopy as well. This enables navigation on the sample and reduces the size of the area under investigation in ARPES down to a few micrometers in diameter. This combination of large acceptance angle, high angular resolution and small acceptance area, makes this instrument the ideal tool for electronic structure studies on small samples or sample areas. The design is compact with a straight optical axis. Operation modes are \((k_x, k_y, E_z)\) data acquisition by operation in energy filtered \(k\)-space imaging, (ToF-)PEEM mode, energy-filtered real space imaging and micro-spectroscopy mode.

The 3D \((k_x, k_y, E_z)\) data recording is done with a 2-dimensional delayline detector, with a time resolution of 150 ps and count rates up to 8 Mcps. It uses channelplates with 40 μm spatial resolution. While the \(x,y\) position of an incoming electron is converted into \(k_x, k_y\) wave vector, the kinetic energy \(E_z\) is determined from the flight time \(t\) in METIS or obtained directly by the energy filter in KREIOS. Spin-resolved imaging is achieved by electron reflection at a W(100) spin-filter crystal prior to the 2-dimensional delayline detector. Electrons are reflected in the [010] azimuth at 45° reflection angle. Varying the scattering energy one can choose positive, negative, or vanishing reflection asymmetry.

Besides a description on how the instruments work data from both instruments on different single crystalline materials will be presented.

11:00am **SA+AC+MI-ThM-10 X-ray Photon Correlation Spectroscopy Studies of Soft Matter and Biomaterials, Laurence B. Lurio, Northern Illinois University, Unites states**

The use of x-ray photon correlation spectroscopy to study dynamics in soft materials and bio-materials will be reviewed. Examples will be presented from the dynamics of colloidal suspensions, polymers and concentrated proteins.

11:40am **SA+AC+MI-ThM-12 Forefront Applications of XPCS, Anders Madsen, European XFEL GmbH, Germany**

Recent advances in dynamics studies of condensed matter by X-ray photon correlation spectroscopy (XPCS) require a (partially) coherent beam and a reliable detector and has benefitted a lot from recent synchrotron source upgrades and the advent of novel 2D pixel detectors. Weakly scattering systems and fast dynamics can now be characterized much better than only a few years back. The next generation of X-ray sources - X-ray Free-Electron Lasers (XFEL) - will deliver many orders of magnitude more coherent intensity than the present generation of synchrotrons but at the same time the pulsed nature of XFELs requires new XPCS-like techniques to be developed. In the presentation I discuss a few new methods that take advantage of the XFEL pulse pattern and allow dealing with the pertinent problem of beam induced damage to the samples. Examples of Scientific applications in soft- and hard-condensed matter will be given as well as an outlook to the forthcoming European XFEL facility where time-resolved coherent X-ray experiments will be carried out at the MID station.
## Author Index

<table>
<thead>
<tr>
<th>Author</th>
<th>Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liu, J.</td>
<td>SA+AS+HC+SS+Wea-1, 27</td>
</tr>
<tr>
<td>Liu, Y.</td>
<td>Mi+SA+Mi+SA-Tua-4, 13</td>
</tr>
<tr>
<td>Liu, Z.</td>
<td>Hc+SA+SS-Wea-7, 25</td>
</tr>
<tr>
<td>Locatelli, A.</td>
<td>SA+AS+HC+SS+Wea-1, 27</td>
</tr>
<tr>
<td>Lockart, M.</td>
<td>Mi+BM+EM+SA-Moa-5, 6</td>
</tr>
<tr>
<td>Lörhner, F.</td>
<td>SA+AS+HC+SS+Wea-12, 28</td>
</tr>
<tr>
<td>Long, J.</td>
<td>AC+AS+SA-Tua-10, 8</td>
</tr>
<tr>
<td>Lopez, J.</td>
<td>SA+HC+SS-Tua-12, 26</td>
</tr>
<tr>
<td>Lu, Z.</td>
<td>2D+AS+SP-Tua-10, 6</td>
</tr>
<tr>
<td>Luening, J.</td>
<td>SA+AC+Mi-Thm-3, 34</td>
</tr>
<tr>
<td>Lundqvist, M.</td>
<td>SA-Tup-3, 17</td>
</tr>
<tr>
<td>Luque, F.</td>
<td>Mi+BM EM+SA-Moa-3, 4</td>
</tr>
<tr>
<td>Lucio, L.</td>
<td>SA+AC+Mi-Thm-10, 35</td>
</tr>
<tr>
<td>Ma, T.</td>
<td>HC+SA+SS-Wea-2, 25</td>
</tr>
<tr>
<td>Machado, Á.</td>
<td>AS+2D+NS+SA-Wea-12, 24</td>
</tr>
<tr>
<td>Mack, P.</td>
<td>Mi+BM+NS+SA+SS-Wee-2, 18</td>
</tr>
<tr>
<td>Mådler, D.</td>
<td>Mi+BM EM+SA-Moa-4, 4</td>
</tr>
<tr>
<td>Malandona, P.</td>
<td>Mi+AC+Mi+SA-MoM-8, 2</td>
</tr>
<tr>
<td>Mandrefa, M.</td>
<td>AC+MI+AC+MI-Thm-3, 34</td>
</tr>
<tr>
<td>Mann, B.</td>
<td>Mi+SA+AS-Thm-5, 31</td>
</tr>
<tr>
<td>Mao, M.</td>
<td>SA+AS+HC+SS-Wea-1, 27</td>
</tr>
<tr>
<td>Marcos, T.</td>
<td>Mi+SA-Wee-13, 21</td>
</tr>
<tr>
<td>Marsh, B.</td>
<td>SA+Mi-Thm-12, 10</td>
</tr>
<tr>
<td>Martinez, E.</td>
<td>SA+AS+HC+SS-Tua-10, 15</td>
</tr>
<tr>
<td>Martinez, M.</td>
<td>SA+AS+HC+SS-Tua-12, 16</td>
</tr>
<tr>
<td>Masarache, A.</td>
<td>Mi+BM EM+SA-Moa-5, 4</td>
</tr>
<tr>
<td>Maskova, K.</td>
<td>SA+AC+AC+MI-Thm-3, 34</td>
</tr>
<tr>
<td>Mason, J.</td>
<td>AC+SA+SS+MoM-10, 3</td>
</tr>
<tr>
<td>Matej, Z.</td>
<td>AC+AS+SA-MoM-10, 3</td>
</tr>
<tr>
<td>Mazzoli, Y.</td>
<td>2D+NS+SA-Wea-3, 23</td>
</tr>
<tr>
<td>McBibbin, S.</td>
<td>SA+HC+SS-Tua-3, 14</td>
</tr>
<tr>
<td>Meng, X.</td>
<td>SA+HC+SS-Wea-11, 26</td>
</tr>
<tr>
<td>Mentes, T.</td>
<td>SA+AC+SS-Wea-9, 28</td>
</tr>
<tr>
<td>Menzel, S.</td>
<td>SA+HC+SS-Wea-7, 27</td>
</tr>
<tr>
<td>Michael, K.</td>
<td>Mi+BM EM+SA-Moa-1, 4</td>
</tr>
<tr>
<td>Michel, E.</td>
<td>Mi+BM EM+SA-Moa-5, 4</td>
</tr>
<tr>
<td>Middleburgh, S.</td>
<td>AC+Mi+AC+MI-MoM-4, 1</td>
</tr>
<tr>
<td>Mikkelson, A.</td>
<td>SA+AC+HC+SS-Tua-3, 14</td>
</tr>
<tr>
<td>Miliyanchuk, K.</td>
<td>Mi+AC+MI+SA-MoM-4, 1</td>
</tr>
<tr>
<td>Minasian, S.</td>
<td>AC+SA+SS-Tua-10, 8</td>
</tr>
<tr>
<td>Misha, A.</td>
<td>SA+HC+SS-Tua-12, 16</td>
</tr>
<tr>
<td>Moffitt, C.</td>
<td>Mi+SA+THm-3, 31</td>
</tr>
<tr>
<td>Mohite, A.</td>
<td>2D+AC+SP-Tua-6, 6</td>
</tr>
<tr>
<td>Möllers, P.</td>
<td>Mi+SA-Them-13, 21</td>
</tr>
<tr>
<td>Monroe, J.</td>
<td>Bi+SA+SH-Tua-10, 32</td>
</tr>
<tr>
<td>Moségui González, D.</td>
<td>Mi+SA-Thm-6, 10</td>
</tr>
<tr>
<td>Mottaghi, N.</td>
<td>Mi+2D+AC+SA+SS-Tua-12, 9</td>
</tr>
<tr>
<td>Mouton, I.</td>
<td>AS+2D+NS+SA-Wea-3, 23</td>
</tr>
<tr>
<td>Müllner, B.</td>
<td>SA+A+AC+Mi-Thm-3, 34</td>
</tr>
<tr>
<td>Müller-Buschbaum, P.</td>
<td>SA+AC+MI-Thm-12, 28, 8+SA+MI-Thm-3, 10</td>
</tr>
<tr>
<td>Müller-Renno, C.</td>
<td>Bi+AS+MI+SA-Tua-3, 13</td>
</tr>
<tr>
<td>Múncho, J.</td>
<td>SA+HC+SS-Tua-12, 16</td>
</tr>
<tr>
<td>Murković, R.</td>
<td>HC+SA+SS-Wea-1, 25</td>
</tr>
<tr>
<td>Naaman, R.</td>
<td>Mi+SA-Them-13, 21</td>
</tr>
<tr>
<td>Nakashishi, M.</td>
<td>Mi+2D+AC+SA+SS-Wea-5, 7</td>
</tr>
<tr>
<td>Nakatsuka, N.</td>
<td>SA+MI-Wea-5, 20</td>
</tr>
<tr>
<td>Nathanson, S.</td>
<td>Mi+AC+SS+Wea-3, 25</td>
</tr>
<tr>
<td>Nelson, A.</td>
<td>AC+AS+MI-Thm-4, 7</td>
</tr>
<tr>
<td>Nemšák, S.</td>
<td>SA+HC+SS+Wea-3, 27</td>
</tr>
<tr>
<td>Newberg, J.</td>
<td>Bi+SA+SS+Thm-5, 29</td>
</tr>
<tr>
<td>Ngo, C.</td>
<td>AS+2D+NS+SA-Wea-11, 24</td>
</tr>
<tr>
<td>Nilsson, A.</td>
<td>SA+AC+MI+MI-Thm-1, 21</td>
</tr>
<tr>
<td>Niño, M.</td>
<td>Mi+BM EM+SA-Moa-3, 4</td>
</tr>
<tr>
<td>Nollet, E.</td>
<td>2D+AS+NS+SA-Wea-3, 23</td>
</tr>
<tr>
<td>Nordlund, D.</td>
<td>AC+SA+SA-MoM-1, 3</td>
</tr>
<tr>
<td>Novotny, Z.</td>
<td>2D+AS+AC+MI-Thm-12, 30</td>
</tr>
<tr>
<td>Oberg, G.</td>
<td>Mi+AC+MI+NS+SA+SS-Wea-3, 18</td>
</tr>
<tr>
<td>Olhausen, J.</td>
<td>Bi+Mi+MN+SA+SS+Wea-M-12, 19</td>
</tr>
<tr>
<td>Ohm, W.</td>
<td>SA+AC+Mi-Thm-5, 34</td>
</tr>
<tr>
<td>Ohta, T.</td>
<td>2D+AS+SP-Tua-M-6, 6</td>
</tr>
<tr>
<td>Okamoto, S.</td>
<td>Mi+BM EM+SA-Moa-4, 4</td>
</tr>
<tr>
<td>Olzsa, M.</td>
<td>AS+2D+NS+SA-Wea-7, 23</td>
</tr>
<tr>
<td>Oppeneer, P.</td>
<td>AC+Mi+SA+SA+MoM-8, 2</td>
</tr>
<tr>
<td>Orlando, F.</td>
<td>Bi+SA+SH+SS-Thm-12, 30</td>
</tr>
<tr>
<td>Osgood, R.</td>
<td>2D+AS+SP-Tua-M-1, 6</td>
</tr>
<tr>
<td>Ostrowski, J.</td>
<td>AS+2D+NS+SA-Wea-10, 24</td>
</tr>
<tr>
<td>Osterwalder, J.</td>
<td>Bi+SA+SS+Thm-12, 30</td>
</tr>
<tr>
<td>Ouladjaib, M.</td>
<td>AC+MI+SM+SMoM-3, 1</td>
</tr>
<tr>
<td>Ouyang, W.</td>
<td>AS+2D+NS+SA-Wea-2, 23</td>
</tr>
<tr>
<td>Öztürk, E.</td>
<td>AC+AS+SA-Tua-11, 8</td>
</tr>
<tr>
<td>Packholski, M.</td>
<td>AS+2D+NS+SA-Wea-2, 23</td>
</tr>
<tr>
<td>Palmgren, P.</td>
<td>SA-Tup-3, 17</td>
</tr>
<tr>
<td>Palltiel, Y.</td>
<td>Mi+BM EM+SA-Moa-10, 5</td>
</tr>
<tr>
<td>Pangan, C.</td>
<td>SA+AC+Mi-Thm-3, 34</td>
</tr>
<tr>
<td>Pelster, A.</td>
<td>AS+2D+NS+SA-Wea-1, 23</td>
</tr>
<tr>
<td>Perez, L.</td>
<td>Mi+BM EM+SA-Moa-M-8, 2</td>
</tr>
<tr>
<td>Petrovykh, D.</td>
<td>Bi+AS+SA-Them-12, 32</td>
</tr>
<tr>
<td>Piekarz, A.</td>
<td>Mi+AC+MI+SA-Tua-9, 12</td>
</tr>
<tr>
<td>Pietsch, U.</td>
<td>SA+AC+MI-Thm-3, 34</td>
</tr>
<tr>
<td>Pinto, J.</td>
<td>Bi+SA+THm-12, 32</td>
</tr>
<tr>
<td>Pirzini, S.</td>
<td>SA+HS+SS-Wea-9, 28</td>
</tr>
<tr>
<td>Plakhova, T.</td>
<td>AC+AS+SA-Tua-10, 8</td>
</tr>
<tr>
<td>Poleius, C.</td>
<td>AS+Bi+MI+NS+SA+SS+We-6, 18</td>
</tr>
<tr>
<td>Polonsky, O.</td>
<td>SA+AC+HC+SS-Wea-12, 28</td>
</tr>
<tr>
<td>Powell, B.</td>
<td>AC+AS+SA-Tua-5, 8</td>
</tr>
<tr>
<td>Priebé, A.</td>
<td>AS+2D+NS+SA-Wea-3, 23</td>
</tr>
<tr>
<td>Prodi, A.</td>
<td>AC+MI+SM+SMoM-8, 2</td>
</tr>
<tr>
<td>Pröll, S.</td>
<td>HC+SA+Thm-12, 32</td>
</tr>
<tr>
<td>Pylypenko, S.</td>
<td>AS+2D+NS+SA-Wea-11, 24</td>
</tr>
<tr>
<td>Ritter, T.</td>
<td>Bi+SA+SS+Thm-3, 39</td>
</tr>
<tr>
<td>Radder, S.</td>
<td>SA+BI+SS+Thm-6, 29</td>
</tr>
</tbody>
</table>

## Bold pages indicate presenter
### Author Index

<table>
<thead>
<tr>
<th>Author</th>
<th>Affiliations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun, X</td>
<td>2D+AS+SA+SP</td>
</tr>
<tr>
<td>Strelcov, E</td>
<td>SA+AS+HC+SS</td>
</tr>
<tr>
<td>Stock, P</td>
<td>BI+AS+SA</td>
</tr>
<tr>
<td>Shiflett, M</td>
<td>AS+BI+SA+SS</td>
</tr>
<tr>
<td>Severo Pereira Gomes, A</td>
<td>AC+MI+SA+SU</td>
</tr>
<tr>
<td>Schulmeyer, T</td>
<td>SA+AC+MI</td>
</tr>
<tr>
<td>Schoenhense, G</td>
<td>SA+AC+MI</td>
</tr>
<tr>
<td>Schoen, D</td>
<td>SA+AS+HC+SS</td>
</tr>
<tr>
<td>Schmitz, C</td>
<td>SA+AS+HC+SS</td>
</tr>
<tr>
<td>Schlegel, C</td>
<td>BI+AS+SA</td>
</tr>
<tr>
<td>Russell, T</td>
<td>SA+MI</td>
</tr>
<tr>
<td>TuA, Gómez, S</td>
<td>MI+BI+EM+SA</td>
</tr>
<tr>
<td>WeM, 3, 25</td>
<td>-</td>
</tr>
<tr>
<td>ThM, 6, 5</td>
<td>-</td>
</tr>
<tr>
<td>TuM, 10, 32</td>
<td>-</td>
</tr>
<tr>
<td>Walkup, D</td>
<td>MI+2D+AC+SA+SS</td>
</tr>
<tr>
<td>Wadayama, T</td>
<td>HC+SA+SS-Wea-1</td>
</tr>
<tr>
<td>Vurpillot, F</td>
<td>AS+2D+NS+SA</td>
</tr>
<tr>
<td>von Gundlach, A</td>
<td>BI+AS+MI+SA</td>
</tr>
<tr>
<td>Veillerot, M</td>
<td>SA+AS+HC+SS</td>
</tr>
<tr>
<td>Vaz, C</td>
<td>MI+SA</td>
</tr>
<tr>
<td>TuA, C</td>
<td>AC+AS+SA+SU</td>
</tr>
<tr>
<td>Turek, I</td>
<td>AC+AS+SA+SU</td>
</tr>
<tr>
<td>Timm, R</td>
<td>-</td>
</tr>
<tr>
<td>Tao, C</td>
<td>MI+2D+SA+SP-Wea-10, 6</td>
</tr>
<tr>
<td>Tassini, F</td>
<td>MI+SA-Wea-13, 21</td>
</tr>
<tr>
<td>Taylor, M</td>
<td>BI+SA+THM-1, 30; BI+AS+THM-5, 31</td>
</tr>
<tr>
<td>Tempe, A</td>
<td>BI+2D+NS+SA-Wea-3, 23</td>
</tr>
<tr>
<td>Thissen, A</td>
<td>MI+AC+MI-THM-6, 35</td>
</tr>
<tr>
<td>Thornton, G</td>
<td>SA+MI-TU-13, 11</td>
</tr>
<tr>
<td>Tian, G</td>
<td>AC+AS+SA-TU-10, 8</td>
</tr>
<tr>
<td>Timm, R</td>
<td>SA+HC+SS-TU-3, 14</td>
</tr>
<tr>
<td>Tobin, J</td>
<td>AC+AS+SA-MoA-1, 3</td>
</tr>
<tr>
<td>Todoroki, N</td>
<td>HC+SA+SS-Wea-1, 25</td>
</tr>
<tr>
<td>Torres, A</td>
<td>SA-TU-2, 17</td>
</tr>
<tr>
<td>Tougaard, S</td>
<td>SA-TU-2, 17</td>
</tr>
<tr>
<td>Trappen, R</td>
<td>MI+2D+AC+SA+SS-TU-12, 9</td>
</tr>
<tr>
<td>Trenany, M</td>
<td>HC+SA+SS-THM-2, 33</td>
</tr>
<tr>
<td>Trojan, A</td>
<td>SA+AS+HC+SS-TU-3, 14</td>
</tr>
<tr>
<td>Turano, M</td>
<td>HC+SA+SS-Wea-10, 26</td>
</tr>
<tr>
<td>Turek, I</td>
<td>AC+AS+SA-MoA-2, 3</td>
</tr>
<tr>
<td>Turkmen, Y</td>
<td>BI+SA+THM-4, 29</td>
</tr>
<tr>
<td>Tusche, C</td>
<td>SA+AC+MI-THM-6, 35</td>
</tr>
<tr>
<td>Tyler, B</td>
<td>AC+2D+NS+SA-Wea-1, 23</td>
</tr>
<tr>
<td>Tyliszczak, T</td>
<td>AC+AS+SA-MoA-1, 3</td>
</tr>
<tr>
<td>Tyliszczak, T</td>
<td>AC+AS+SA-TU-10, 8</td>
</tr>
<tr>
<td>Utber, R</td>
<td>SA+MI+THM-6, 31</td>
</tr>
<tr>
<td>Ulght, B</td>
<td>BI+SA+SS-THM-4, 29</td>
</tr>
<tr>
<td>Uzlig, T</td>
<td>BI+SA+THM-10, 32</td>
</tr>
<tr>
<td>Uyaner, M</td>
<td>AC+AS+SA-TU-11, 8</td>
</tr>
<tr>
<td>Vaida, M</td>
<td>SA+MI-TU-12, 10</td>
</tr>
<tr>
<td>Valeriano, W</td>
<td>AC+2D+NS+SA-Wea-12, 24</td>
</tr>
<tr>
<td>Vallet, V</td>
<td>AC+MI+SA+TU-3, 12</td>
</tr>
<tr>
<td>Valtiner, M</td>
<td>BI+SA+THM-10, 32</td>
</tr>
<tr>
<td>van der Laan, G</td>
<td>AC+AS+SA-MoA-1, 3</td>
</tr>
<tr>
<td>Van Humbeck, J</td>
<td>AC+AC+SA-TU-10, 8</td>
</tr>
<tr>
<td>Vasclo, J</td>
<td>AS+2D+NS+SA-Wea-12, 24</td>
</tr>
<tr>
<td>Vaz, C</td>
<td>MI+SA-Wea-10, 20</td>
</tr>
<tr>
<td>Veillerot, M</td>
<td>SA+AS+HC+SS-TU-10, 15</td>
</tr>
<tr>
<td>Vianco, P</td>
<td>AS+BI+NS+SA+SS-Wea-12, 19</td>
</tr>
<tr>
<td>Vidal, V</td>
<td>SA+AS+HC+SS-TU-12, 16</td>
</tr>
<tr>
<td>Viro, T</td>
<td>AC+MI+SA-TU-3, 12</td>
</tr>
<tr>
<td>Vlasak, P</td>
<td>AS+BI+MI+NS+SA+SS-Wea-5, 18</td>
</tr>
<tr>
<td>Vogel, J</td>
<td>SA+AS+HC+SS-Wea-9, 28</td>
</tr>
<tr>
<td>von Gundlach, A</td>
<td>BI+AS+MI+SA-TU-11, 14</td>
</tr>
<tr>
<td>Vorng, J</td>
<td>BI+AS+MI+SA-TU-10, 13</td>
</tr>
<tr>
<td>Vurpillot, F</td>
<td>AS+2D+NS+SA-Wea-3, 23</td>
</tr>
<tr>
<td>Wadayaama, T</td>
<td>HC+SA+SS-Wea-1, 25</td>
</tr>
<tr>
<td>Walkup, D</td>
<td>MI+2D+AC+SA+SS-TU-2, 8</td>
</tr>
<tr>
<td>Waluyo, I</td>
<td>AS+BI+SA+SS-THM-3, 12</td>
</tr>
<tr>
<td>Wang, C</td>
<td>AS+2D+NS+SA-Wea-7, 23; SA+MI-TU-6, 10</td>
</tr>
<tr>
<td>Wang, J</td>
<td>AS+BI+MI+NS+SA+SS-Wea-13, 19</td>
</tr>
<tr>
<td>Wang, S</td>
<td>AC+AS+SA-TU-10, 8</td>
</tr>
<tr>
<td>Wang, Y</td>
<td>2D+SA+SP-TU-11, 7</td>
</tr>
<tr>
<td>Waser, R</td>
<td>SA+AS+HC+SS-Wea-7, 27</td>
</tr>
<tr>
<td>Watanebe, K</td>
<td>MI+2D+AC+SA+SS-TU-2, 8</td>
</tr>
<tr>
<td>Widowik, U</td>
<td>AC+MI+SA+SU-Wea-9, 12</td>
</tr>
<tr>
<td>Weaver, J</td>
<td>HC+SA+SS-THM-12, 34</td>
</tr>
<tr>
<td>Weiland, C</td>
<td>SA+AS+HC+SS-TU-9, 15</td>
</tr>
<tr>
<td>Weiss, A</td>
<td>AC+AS+SA-TU-3, 7</td>
</tr>
<tr>
<td>Weiss, P</td>
<td>MI+SA-Wea-5, 20</td>
</tr>
<tr>
<td>Weng, T</td>
<td>AC+AS+SA+SU-MoA-1, 3</td>
</tr>
<tr>
<td>Werner, C</td>
<td>BI+MI+SA-TU-1, 12</td>
</tr>
<tr>
<td>White, M</td>
<td>HC+SA+SS-Wea-11, 26</td>
</tr>
<tr>
<td>Wiel, T</td>
<td>SA-TU-3, 17</td>
</tr>
<tr>
<td>Wiesttruk, M</td>
<td>SA+AC+MI-THM-6, 35</td>
</tr>
<tr>
<td>Wilhelm, F</td>
<td>MI+2D+AC+SA+SS-TU-6, 9</td>
</tr>
<tr>
<td>Woicik, J</td>
<td>SA+AS+HC+SS-TU-9, 19</td>
</tr>
<tr>
<td>Wörle, M</td>
<td>SA+AC+MI+THM-5, 34</td>
</tr>
<tr>
<td>Y —</td>
<td>Yaita, T</td>
</tr>
<tr>
<td>Yamashita, Y</td>
<td>SA-TU-2, 17</td>
</tr>
<tr>
<td>Yang, H</td>
<td>MI+2D+AC+SA+SS-Wea-3, 8</td>
</tr>
<tr>
<td>Yang, P</td>
<td>AC+MI+SA+SU-MoM-5, 1</td>
</tr>
<tr>
<td>Yang, Y</td>
<td>BI+MI+SA-TU-11, 14</td>
</tr>
<tr>
<td>Ye, M</td>
<td>MI+SA-Wea-5, 20</td>
</tr>
<tr>
<td>Yi, J</td>
<td>MI+BI+EM+SA-MoA-4, 4</td>
</tr>
<tr>
<td>Yngman, S</td>
<td>SA+AS+HC+SS-TU-3, 14</td>
</tr>
<tr>
<td>Yoshigoe, A</td>
<td>AS+BI+SA+THM-11, 30; SA+AS+HC+SS-Wea-11, 28</td>
</tr>
<tr>
<td>Yousefi Sarraf, S</td>
<td>MI+2D+AC+SA+SS-TU-12, 9</td>
</tr>
<tr>
<td>Yu, S</td>
<td>AC+AS+SA+SU-MoA-1, 3</td>
</tr>
<tr>
<td>Yu, X</td>
<td>AS+BI+MI+NS+SA+SS-Wea-1, 18</td>
</tr>
<tr>
<td>Zhang, J</td>
<td>MI+2D+NS+SA+SS-Wea-13, 19; BI+AS+SA-TU-13, 32</td>
</tr>
<tr>
<td>Yulaev, A</td>
<td>SA+AS+HC+SS-Wea-3, 27</td>
</tr>
<tr>
<td>— Z —</td>
<td>Zaba, T</td>
</tr>
<tr>
<td>Zabel, H</td>
<td>SA+AC+MI+THM-3, 34</td>
</tr>
<tr>
<td>Zakba, W</td>
<td>AS+BI+SA+SS-TU-12, 30</td>
</tr>
<tr>
<td>Zacharias, H</td>
<td>MI+SA-Wea-12, 21; MI+SA-Wea-13, 21</td>
</tr>
<tr>
<td>Zbrowski, C</td>
<td>SA-TU-2, 17</td>
</tr>
<tr>
<td>Zeigermann, P</td>
<td>SA-TU-3, 17</td>
</tr>
<tr>
<td>Zhai, Z</td>
<td>AS+2D+NS+SA-Wea-7, 23</td>
</tr>
<tr>
<td>Zhang, C</td>
<td>BI+AS+MI+SA-TU-4, 13</td>
</tr>
<tr>
<td>Zhang, D</td>
<td>HC+SA+SS-Thm-3, 33</td>
</tr>
<tr>
<td>Zhang, F</td>
<td>2D+SA+SP-TU-10, 6; AS+BI+MI+NS+SA+SS-Wea-1, 18</td>
</tr>
<tr>
<td>Zhang, H</td>
<td>2D+SA+SP-TU-5, 6; SA+AS+HC+SS-Wea-1, 27</td>
</tr>
<tr>
<td>Zhang, Y</td>
<td>AS+BI+MI+NS+SA+SS-Wea-13, 19; SA+MI-TU-13, 11</td>
</tr>
<tr>
<td>Zheng, H</td>
<td>2D+AS+SP-TU-10, 6</td>
</tr>
<tr>
<td>Zhitenev, N</td>
<td>MI+2D+AC+SA+SS-TU-2, 8</td>
</tr>
<tr>
<td>Zhu, C</td>
<td>SA+MI-TU-6, 10</td>
</tr>
<tr>
<td>Zhu, Z</td>
<td>AS+BI+MI+NS+SA+SS-Wea-1, 18; AS+BI+MI+NS+SA+SS-Wea-13, 19</td>
</tr>
<tr>
<td>Ziegler, C</td>
<td>BI+AS+MI+SA-TU-3, 13; BI+AS+SA-TU-6, 31</td>
</tr>
<tr>
<td>Zou, Q</td>
<td>MI+BI+EM+SA-MoA-4, 4</td>
</tr>
</tbody>
</table>