

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

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

Moderator: Tomasz Durakiewicz, Los Alamos National Laboratory

8:20am AC+MI+SA+SU-MoM-1 Magnetic and Transport Characteristics in the Uranium Intermetallic Compounds with the HoCoGa₅-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 HoCoGa₅-type structure have extensively been studied because of unusual correlated electronic states, including heavy effective mass of conduction electrons, magnetic orderings 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 URhX₅ (X = Ga and In). While URhIn₅ orders antiferromagnetically at fairly high temperature 98 K, isostructural and formally isoelectronic analogue URhGa₅ 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.

[1] Y. Matsumoto et al., Phys. Rev. B 88, 045120 (2013).

[2] S. Ikeda et al., Physica B 359-361, 1039 (2005).

[3] Y. Matsumoto et al, JPS Conf. Proc. 3, 011097 (2014).

9:00am AC+MI+SA+SU-MoM-3 Magnetic Structures of Layered U_nRhIn_{3n+2} Materials, Attila Bartha, M Klicpera, Charles University, Prague, Czech Republic; P Čermák, Forschungszentrum Juelich GmbH, Germany; B Ouladdiaf, Institut Laue Langevin, France; P Javorský, 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 electronics. 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 metal. Another example is high temperature superconductors being quasi-2D materials 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 Ce_nT_mIn_{3n+2m} (*n*=1, 2; *m*=0, 1, 2; T=transition metal) of layered compounds, which can be viewed as *m* TIn₂-layers alternating with *n*-layers of CeIn₃ along the *c*-axis, has been extensively investigated. CeIn₃ is cubic (3D) and orders antiferromagnetically (AFM) at *T_N* = 10.2 K [1] with a propagation vector **k** = (0.5, 0.5, 0.5) [2]. Under hydrostatic pressure superconductivity appears with highest *T_c* = 0.3 K at *p* = 2.5 GPa. In CeRhIn₅, the anisotropic crystal structure leads to an incommensurate magnetic structure described with **k** = (0.5, 0.5, 0.297). The AFM order is reduced (*T_N* = 3.8 K) while superconductivity is supported, *T_c* increases to 1.9 K at *p* = 1.77 GPa [3-4].

We report on the magnetic structures of URhIn₅ and U₂RhIn₈, two new members of this intriguing R_nT_mX_{3n+2m} (R= Lanthanide, Actinide, X = In, Ga) family of compounds. Neutron diffraction measurements were performed on structurally well-defined single crystals. Both, URhIn₅ and U₂RhIn₈, adopt the tetragonal Ho_nCoGa_{3n+2}-type structure (P4/*mmm*) typical for this group of compounds. URhIn₅ orders antiferromagnetically below *T_N* = 98 K. The propagation vector equals **k** = (0.5, 0.5, 0.5) and we obtained a value of 1.65 μ_B/U³⁺ 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 μ_B/U³⁺. 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.

[1] C. Pfeleiderer, Rev. Mod. Phys. 81 (2009) 1551

[2] A Benoit et al., Solid State Commun. 34 (1980) 39

[3] H. Shishido et al. J. Phys. Soc. Jpn. Vol. 71 Suppl. (2002) 276

[4] H. Hegger et al., Phys. Rev. Lett. 84 (2000) 4986

9:20am AC+MI+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 Middleburgh, Westinghouse Electric Sweden AB, Vasteras, Sweden; L Havela, Charles University, Prague, Czech Republic

U₃Si₂ (tetragonal structure with the space group of P4/*mbm* 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 U₃Si₂H_{1.8}. 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 - U₃Si tetrahedra (similar to U₃T tetrahedra in U₂T₃X compounds [3] crystallizing in an ordered ternary derivative of the U₃Si₂ structure) and a split position in the U₆ octahedra consisting of 4 U1 and 2 U2 atoms (H atom shifts from the central position into the tetrahedra formed by 2 U1 and 2 U2 atoms. As H generally does not occupy two adjacent tetrahedra, we can assume only two from the 4 tetrahedra occupied). The later 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 U₃Si₂H_{1.8} shows an upturn and a dramatic enhancement of the Sommerfeld coefficient of electronic specific heat γ, which reaches 440 mJ/mol f.u. K² (γ = 88 mJ/mol f.u. K² for U₃Si₂).

This work was supported by The Czech Science Foundation under the Grant No. 15-01100S.

[1] K.D. Johnson, A.M. Raftery, D.A. Lopes, J. Wallenius, J. Nucl. Mater. 477 (2016) 18-23.

[2] E. Sooby Wood, J.T. White, A.T. Nelson, J. Nucl. Mater. 484 (2017) 245-257.

[3] K. Miliyanchuk, L. Havela, A.V. Kolomiets, A.V. Andreev, Physica B 359-361 (2005) 1042-1044.

[4] T. Miyadai, H. Mori, T. Oguchi, Y. Tazuke, H. Amitsuka, T. Kuwai and Y. Miyako, J. Magn. Magn. Mater. 104-107 (1992) 47-48.

9:40am AC+MI+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.

Monday Morning, October 30, 2017

10:40am **AC+MI+SA+SU-MoM-8 Inelastic X-ray Scattering Study of the Crystal Dynamics of Neptunium and Uranium Dioxide, Roberto Caciuffo**, European Commission, Joint Research Centre, Karlsruhe, Germany; *P Maldonado*, Uppsala University, Sweden; *L Paolasini*, European Synchrotron Radiation Facility, France; *P Oppeneer*, Uppsala University, Sweden; *T Forrest*, European Synchrotron Radiation Facility, France; *A Prodi*, Consiglio Nazionale delle Ricerche, Italy; *N Magnani*, European Commission, Joint Research Centre, Karlsruhe, Germany; *A Bosak*, European Synchrotron Radiation Facility, France; *G Lander*, European Commission, Joint Research Centre, Karlsruhe, Germany **INVITED**

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 $0.4 \times 0.3 \times 0.3 \text{ mm}^3$ 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 .

[1] P. Maldonado *et al.*, Phys Rev B **93**, 144301 (2016)

11:20am **AC+MI+SA+SU-MoM-10 Emergent Phenomena in 4f Heavy-Fermion Systems: from Bulk to Thin-Films, Priscila Rosa**, Los Alamos National Laboratory **INVITED**

The interplay between magnetism and unconventional superconductivity in bulk materials has been one of the central topics in condensed matter physics for the past 40 years. In particular, the family of compounds CeMIn_5 ($M = \text{Co, Rh, Ir}$) provides an ideal platform for such investigation due to the small energy scales involved, and the high sample quality. In this talk, I will first discuss novel insights provided by substitution studies in bulk CeRhIn_5 under pressure. I will then present recent efforts to fabricate hybrid superlattices consisting of alternating superconducting CeCoIn_5 and antiferromagnetic CeRhIn_5 .

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 Tylliszczak*, 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 includes the utilization 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 (UO₂), uranium trioxide (UO₃), and uranium tetrafluoride (UF₄). 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 UO₂ and UF₄ are n_{5f} = 2 materials. The combination of the 4d XAS BR and RXES analyses is particularly powerful. (3) CF broadening in the L₃ RXES spectroscopy does not preclude a successful analysis. (4) The prior experimental result that n_{5f} (UO₂) = 3 and the proposed causation by covalent bonding was incorrect. UO₂ is an n_{5f} = 2 material and analysis within a simple, ionically localized picture provides the correct result. (5) UO₃ appears to be an n_{5f} = 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. Tylliszczak, 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 UH₃ 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 UH₃ and (UH₃)_{1-x}Mo_x 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 H₂ in Ar ($p_{Ar} = 8 \cdot 10^{-3}$ 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% H₂ concentration, and we assume that this pressure is sufficient to form UH₃. XRD and X-ray reflectivity proved indeed the β -UH₃ structure of deposited films, which were polycrystalline, but highly textured. Ferromagnetism of the UH₃ films has the correct Curie temperature $T_C \approx 165$ K. Magnetic coercivity of the films is enormous, the width of hysteresis loop exceeds 10 T at low temperatures. Details of the valence band observed in UPS reveal a transformation of the triangular emission of the U metal into a sharp feature at the Fermi level accompanied by a broad shoulder around 0.5 eV for the hydride. A distinct development was noticed also for the U-6p states, which become narrower and shift by 1.2 eV to higher BE in the hydride, which can be interpreted as an impact charge transfer from U towards H. Besides photoelectron spectroscopy, the variations of electronic states were monitored also by BIS spectra collected for the 1486.6 eV photon energy. The spectroscopy results are confronted with different types of in-initio calculations.

As U-Mo alloys tend to form nanocrystalline β -UH₃ based hydrides, we were curious about reactive sputter deposition of the U-Mo alloys. We found that the tendency to form hydrides is fast suppressed by Mo for room temperature sputtering (γ -U alloy without H is the product), but

cooling the substrate to 77 K helps to maintain the hydride phase even for even higher Mo concentrations.

This work was supported by the Czech Science Foundation under the grant No. 15-01100S.

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 waste forms for disposal 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-IV, 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, 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 alloys 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 UH₃-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+BI+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+BI+EM+SA-MoA-1 Spin Transport and Polarization in Chiral Molecules: Theory and Possible Applications**, *Karen Michaeli*, Weizmann Institute of Science, Israel **INVITED**

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+BI+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 Kowalik*, 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 molecular orbitals with π character. Theoretical modeling 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.

[1] B. Göhler V. Hamelbeck, T. Z. Markus, M. Kettner, G. F. Hanne, Z. Vager, R. Naaman, and H. Zacharias, *Science* **331**, 894 (2011).

[2] M. Á. Niño, I. A. Kowalik, F. J. Luque, D. Arvanitis, R. Miranda, and J. J. de Miguel, *Adv. Mater.* **26**, 7474 (2014).

2:40pm **MI+BI+EM+SA-MoA-4 Evolving of Soliton Phase in Exfoliated 2D Cr_{1/3}NbS₂ Nanolayers**, *S Tang*, Oak Ridge National Laboratory and Central South University, China, PR China; *J Yi*, *R Fishman*, *S Okamoto*, *Q Zou*, Oak Ridge National Laboratory; *D Mandrus*, University of Tennessee; **Zheng Gai**, Oak Ridge National Laboratory

Cr_{1/3}NbS₂ is an emergent quasi-2D material that has recently been attracting wide attentions. Cr_{1/3}NbS₂ has both chiral helimagnetic behavior and broken inversion symmetry of Cr atoms, the two necessary conditions for creating Dzyaloshinskii–Moriya interaction in skyrmion. Bulk studies show that a nonlinear periodic magnetic state called a soliton lattice exists in the material. By applying microexfoliation techniques, we successfully prepared thin layers of Cr_{1/3}NbS₂ with various thickness from single crystal. When the thickness of Cr_{1/3}NbS₂ layer falls into the range around the pitch of its helimagnetic state, kinks of field dependent magnetization start to evolve. The new phase is studied experimentally and theoretically. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

3:00pm **MI+BI+EM+SA-MoA-5 Tailoring the Chirality of Domain Walls via Interface Modification**, *Arantazu Mascaraque*, *S Ruiz-Gomez*, *M Gonzalez Barrio*, *L Perez*, Universidad Complutense de Madrid, Spain; *G Chen*, *A Schmid*, Lawrence Berkeley National Laboratory; *E Michel*, Universidad Autonoma de Madrid, Spain

The possibility of manipulating magnetic domain walls (DWs) without the intervention of magnetic fields has interest for a wide variety of applications, such as spintronic devices [1]. Applying an electric current to a ferromagnet creates a force that drives the DWs in the direction of the electron motion, the so-called Spin Transfer Torque. However, this effect is weak and high current densities are needed. Recently, it has been discovered that spin accumulation at the edges of a current-carrying non-magnetic material due to the Spin Hall Effect (SHE), can exert a torque on the magnetization of a neighboring magnetic layer [2]. The torque induced by SHE depends on the chirality of the DW and, as most ferromagnetic materials lack a well-defined chirality, the device applications are limited. However, the presence of surfaces and interfaces removes the point-inversion symmetry, giving rise to an additional interaction, the Dzyaloshinskii–Moriya interaction (DMI) that lifts the left-right degeneracy through spin-orbit coupling [3].

In this work, we have modified the interface between the substrate and a non-chiral magnetic layer, in order to investigate in which way DW chirality can be induced and stabilized in the magnetic layer. The experiments were done using the SPLEEM instrument of the Lawrence Berkeley National Laboratory. This microscope can map independently and in real space the three magnetic components of the spin structures. The magnetic system was a (Ni/Co)_n multilayer epitaxially grown on Cu(111). It is well known that magnetic films grown on Cu(111) do not exhibit homo-chiral DWs [4]. We have found that this behavior can be changed by modifying the interface. After introducing a thin metal layer (suitable to induce a high DMI) between the substrate and the magnetic layer, we have found relevant changes in the chirality of the DWs of the magnetic layer. Our results demonstrate that the buffer layer influences the spin texture, which evolves from non-chiral Bloch to homo-chiral Néel DWs.

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[4] G. Chen, et al., Ap. Phys. Lett. 106, 062402 (2015)

3:20pm **MI+BI+EM+SA-MoA-6 Spin Transport in an Electron Conducting Polymer**, **Greg Szulczewski**, *T Sutch, M Lockart, H Chen, P Rupar, M Bowman*, The University of Alabama

We report results from an electron spin resonance (ESR) study to probe the spin-dynamics in the conducting polymer poly {[N, N9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'9'-bithiophene)} or P(NDI2OD-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 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

INVITED

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 to achieve simple spintronics devices utilizing the effect.

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[3] O. Ben Dor, S. Yochelis, S. P. Mathew, R. Naaman, and Y. Paltiel *Nature Communications* **4**, 2256 (2013).

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[5] O. Ben Dor, N. Morali, S. Yochelis, and Y. Paltiel; *Nano letters* **14** 6042 (2014).

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[8] H. Alpern, E. Katzir, S. Yochelis, Y. Paltiel, and O. Millo; *New J. Phys.* **18** 113048 (2016).

[9] O. Ben Dor, S. Yochelis, A. Radko, K. Vankayala, E. Capua, A. Capua, S.-H. Yang, L. T. Baczewski, S. S. P. Parkin, R. Naaman, and Y. Paltiel; *Nature Communications*, **8** 14567 (2017).

4:40pm **MI+BI+EM+SA-MoA-10 Magnetic Nano Platelets based Spin Memory Device Operating at Ambient Temperatures**, **Guy Koplovitz**, The Hebrew University of Jerusalem; *Y Paltiel*, The Hebrew University of Jerusalem, Israel

There is an increasing demand for realizing a simple Si based universal memory device working at ambient temperatures. In principle non-volatile magnetic memory could operate at low power consumption and high frequencies. However, in order to compete with existing memory technology, size reduction and simplification of the used material systems are essential. In our work we use the Chiral Induced Spin Selectivity (CISS) effect along with 30-50nm Ferro-Magnetic Nano Platelets (FMNPs) in order to realize a simple magnetic memory device. The vertical memory is Si compatible, easy to fabricate and in principle can be scaled down to a single nano particle size. Results show clear dual magnetization behavior with threefold enhancement between the one and zero states. The magnetization of the device is accompanied with large avalanche like noise that we ascribe to the redistribution of current densities due to spin accumulation inducing coupling effects between the different nano platelets.

5:00pm **MI+BI+EM+SA-MoA-11 Magnetization Switching in Ferromagnets by Adsorbed Chiral Molecules without Current or External Magnetic Field**, **Oren Ben Dor**^{1,2}, The Hebrew University of Jerusalem, Israel

Ferromagnets are commonly magnetized by either external magnetic fields or spin polarized currents. The manipulation of magnetization by spin-current occurs through the spin-transfer-torque effect, which is applied, for example, in modern magnetoresistive random access memory. However, the current density required for the spin-transfer torque is of the order of $1 \times 10^6 \text{ A} \cdot \text{cm}^{-2}$, or about $1 \times 10^{25} \text{ electrons} \cdot \text{sec}^{-1} \cdot \text{cm}^{-2}$. This relatively high current density significantly affects the devices' structure and performance. Here, we present a new effect – that of magnetization switching of ferromagnetic thin layers that is induced solely by adsorption of chiral molecules. In this case, about 10^{13} electrons per cm^2 are sufficient to induce magnetization reversal. The direction of the magnetization depends on the handedness of the adsorbed chiral molecules. Local magnetization switching is achieved by adsorbing a chiral self-assembled molecular monolayer on a gold-coated ferromagnetic layer with perpendicular magnetic anisotropy. These results present a simple low power magnetization mechanism when operating at ambient conditions.

¹ Falicov Student Award Finalist

² National Student Award Finalist

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 DESC0012704.

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 ultra-high 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.

[1] A. Zandiatashbar, B. Kim, Y. Yoo, and K. Lee, *Microscopy Today* 23(06):26-31 (2015)

[2] P. Gallagher, M. Lee, F. Amet et al., *Nature Comm.* 7 10745 (2016)

8:40am **2D+AS+SA+SP-TuM-3 Surface and Interface Properties of 2D MoS₂ and WS₂ Materials**, *Chia-Seng Chang*, Institute of Physics, Academia Sinica, Taiwan, Republic of China, 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 MS₂ 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 Ajayan*, 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 postulate that the defects in SiO₂ alleviate 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 CPS25859). 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, PR China; *H Zheng*, 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

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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 MoS₂/WS₂ heterostructure grown on SiO₂ using the CVD method. Scanning tunneling microscopy (STM) and spectroscopy (STS) were performed to study the morphology and band structures of both MoS₂ monolayer and MoS₂/WS₂ 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 ± 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 ± 0.020 nm compared with 0.362 ± 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 MoS₂ monolayer, which are similar to the previously reported results on MoS₂/WS₂ heterostructures fabricated through the mechanical exfoliation method.

11:20am 2D+AS+SA+SP-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 HJ-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 (SPEM) 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
INVITED

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 hydroxypyridinone 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 siderocalin 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), IAEC-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 Boblil, Department of Physics, IAEC-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 trapping 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 ²³⁵U 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 μ 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.

In case of large area detector a set of picture will be taken and by stitching 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 ²³⁵U 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 indicate 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 Pu P₁VV/O₂VV, O KLL, and C KLL 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.

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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 **INVITED**

A 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(V)NH₄CO₃(s), Pu(IV)(C₂O₄)₂(s), Pu(III)₂(C₂O₄)₃(s), Pu(IV)O₂(s), Np(IV)O₂(s) and NpO₂NO₃(s). X-ray absorption spectroscopy (XAS) analysis of initially Pu(V)NH₄(CO₃) 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)O₂(s). Thus, there appears to be an auto-reduction of NH₄Pu(V)CO₃(s) to Pu(IV)O₂(s) even under inert conditions. However, solvent extraction on archived and field-deployed sources show the archived source still contains around 40% Pu(V) whereas the same source from a field lysimeter deployed for 2.5 years contained less than 10% of Pu(V). XAS and electron microscopy studies have demonstrated differences between Pu(IV)O₂(s) formed via reduction of Pu(V)O₂NH₄CO₃ and initially Pu(IV)O₂ formed from precipitation of a Pu(IV) solution. The behavior of initially Np(IV)O₂ sources was quite different showing oxidation to Np(V) and subsequent downward transport of more soluble Np(V)O₂⁺. The oxidation of Np(IV)O₂(s) leads to formation of a much more disordered solid phase with a significantly altered morphology than the initial Np(IV)O₂(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*, Lomonsov Moscow State University, Russia; *S Wang*, University of California Berkeley, LBNL; *G Tian*, *S Minasian*, *T Tysliszczak*, Lawrence Berkeley National Laboratory; *T Yaita*, *T Kobayashi*, Japan Atomic Energy Agency; *S Kalmykov*, Lomonsov 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 have been shown to be indefinitely stable 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 pore surfaces and maximum chemical stability. The adsorption of selected metal ions, Sr²⁺, Fe³⁺, Nd³⁺, and Am³⁺, from aqueous solutions employing a carbon-based PAF, BPP-7 (Berkeley Porous Polymer-7) 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 BPP-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 Photoluminescent, Water and Thermostability Properties of SrAl₂O₄ Based Phosphors, Erkul Karacaoglu, E Öztürk**, Karamanoglu Mehmetbey University, Turkey; *M Uyaner*, Selcuk University, Turkey

Aluminate based phosphors (MAl₂O₄, M₄Al₁₄O₂₅, 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=8.82245Å, c=5.15964Å 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 Ghahari, D Walkup, C Gutierrez**, NIST; Maryland NanoCenter UMD; *J Rodriguez-Nieva*, Harvard University; *K Watanabe*, *T Taniguchi*, National Institute for Materials Science, Japan; *L Levitov*, MIT; *N Zhitenev*, *J Stroscio*, 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 Magnetism 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 development 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.

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Due to the unique topology associated with their band structure, two-dimensional (2D) transition metal dichalcogenides (TMDs) such as WSe_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.

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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 Nakanishi*, *S Aspera*, *H Kasai*, National Institute of Technology, Akashi College, Japan; *W Dino*, Osaka University, Japan

We investigated the possibility of employing the polycrystalline αPbO 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 atom, Fe on the structural and electronic properties of the layered αPbO (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 αPbO 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 αPbO [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 αPbO with Fe interstitials where the minority non-bonding *d* states are partially filled, the Zener's ferromagnetic double exchange mechanism may be dominant and stabilizing the ferromagnetic state.

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9:40am **MI+2D+AC+SA+SS-TuM-6 XMCD Quest for Magnetic Proximity Effect in Ferromagnetic Insulator/Non-Magnetic Metal Interfaces**, *Andrei Rogalev*, *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 $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Magnetic Thin Films**, *Mikel Holcomb*, *R Trappen*, *S Kumari*, *N Mottaghi*, *S Yousefi Sarraf*, *C Huang*, *G 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 $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) thin films. Strong 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 Borchers*, *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 ($\text{Fe}_{84}\text{Ga}_{16}$, 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 ($\text{Ni}_{81}\text{Fe}_{19}$ 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.

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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 pricetag for each of these facilities is in the range of 100's 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 light weight 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 morphologies, 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.^{1,4} 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,^{5,6} in-situ studies during printing⁷ and in-operando studies of organic solar cells⁸ are presented.

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9:40am **SA+MI-TuM-6 In situ Characterization of the Structure Formation in Printed Organic Thin Films for Photovoltaic Applications**, *Stephan Prölller*, TU Munich, Germany; *F Liu*, Shanghai Jiao Tong University, PR China; *C Zhu*, Lawrence Berkeley National Laboratory (LBNL); *D Moseguí González*, TU Munich, Germany; *C Wang*, *E Schaible*, *T Russell*, *A Hexemer*, Lawrence Berkeley National Laboratory (LBNL); *P Müller-Buschbaum*, Technische Universität München, Germany; *E Herzig*, University Bayreuth, Germany

The nanomorphology can strongly influence the physical properties of organic thin films. For example, polymer:fullerene blends used in organic solar cells vary significantly in performance depending on the inner film morphology. To allow large-scale production of these devices, control of the nanostructure during the processing of the active layer is important. This firstly needs an understanding of the processes involved during the drying of the film. In a second step we can then manipulate the drying processes to alter the nanostructure. Using an industrial slot-die coater implemented into a synchrotron beamline we have successfully characterized the solidification process of an active layer using grazing incidence small and wide angle X-ray scattering (GISAXS/GIWAXS). Tracking the actual crystallization and aggregation processes on length scales ranging from sub-nanometers to several tens of nanometers reveals how the different growth processes compete with each other leading to the final film morphology. To achieve this, we follow the evolution of the nanostructure with appropriate time-resolution to initially track the solvent removal, followed by the crystallization of the polymer and the aggregation of the fullerene. We find that the morphological evolution can be separated into several subsequent phases that take place independently of the drying speed of the film. The final film morphology, however, depends on the processing speed, because the individual processes compete with each other differently depending on time. Using an environmental control system, we are able to further control the solvent evaporation and hence the structure formation during processing.

S. Prölller, F. Liu, C. Zhu, C. Wang, T.P. Russell, A. Hexemer, P. Müller-Buschbaum, E.M. Herzig, *Advanced Energy Materials*, **6**: 1501580 (2016)

11:00am **SA+MI-TuM-10 Ultrafast X-ray Scattering Studies of Light-induced Processes in 2D Materials**, *A Lindenberg*, *Edbert Sie*, Stanford University **INVITED**

Novel characterization techniques developed over the past two decades have revolutionized our ability to visualize the microscopic, atomic-scale processes that determine the functional properties of materials. The overarching challenge here is that the relevant time-scales and length-scales for these processes are typically 10^{-13} seconds (100 femtoseconds) and 10^{-10} m (1 Å) such that our view of how a material functions is often blurred out in time or in space. In this talk I will describe recent experiments using femtosecond x-ray pulses as a means of probing and manipulating the optoelectronic and structural properties of materials on ultrafast time-scales, as they transform and *in-situ*. I will focus in particular on recent experiments probing dynamic deformations of multilayer transition metal dichalcogenide films on femtosecond and picosecond time-scales. These studies reveal a surprising light-induced nonlinear modulation in the interlayer bonding, associated with manipulation of the Casimir/van der Waals interaction between quasi-2D layers.

11:40am **SA+MI-TuM-12 Monitoring the Non-Metal to Metal Transition and Ultrafast Charge Carrier Dynamics of Supported Clusters by Femtosecond XUV Photoemission Spectroscopy**, *Mihai Vaida*, University of Central Florida; *B Marsh*, *B Lamoureux*, *S Leone*, University of California at Berkeley

Understanding the electronic structure and charge carrier dynamics of supported clusters is extremely important due to their many potential applications in photochemistry and catalysis. Time resolution, surface sensitivity and element specificity are technical ingredients required to investigate ultrafast photoinduced processes of charge migration, localization and recombination at clusters on a solid surface. All these requirements are fulfilled by a new experimental technique based on pump-probe photoemission spectroscopy (PES) in conjunction with femtosecond extreme ultraviolet (XUV) laser pulses that will be presented in this contribution. The ultrafast electron and hole charge state dynamics is investigated by monitoring the ultrafast photoinduced transient charging of the clusters at surface by core level and Fermi level photoelectron spectroscopic shifts.

Gold clusters grown on 10 ML MgO(100)/Mo(100) are investigated as a model system for using static XUV photoemission as a probe of electronic character versus cluster size. As the size of the Au clusters is increased, a

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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 TiO₂ 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 TiO₂, where the related process of electron trapping is important in a broader range of applications (eg resistive 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.

Actinides and Rare Earths Focus Topic

Room 22 - Session AC+MI+SA+SU-TuA

Actinide and Rare Earth Theory

Moderator: Ladislav Havela, Charles University, Czech Republic

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 **INVITED**

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.

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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 Viot*, IRSN, France **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.¹

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 *a posteriori* with the state-interaction RASSI method. Specifically, our results illustrate the complex multi-configurational character of PuO₃. The computed thermodynamics quantities reach a high accuracy allowing us to predict the composition of the released volatile products.

5:00pm AC+MI+SA+SU-TuA-9 The Thermal Expansion of UC and UO₂ from First Principles Calculations - The Importance of Correlations Effects and Spin-orbit Coupling, **Dominik Legut**, IT4Innovations Center, VSB - Technical University of Ostrava, Czech Republic; *U Wdowik*, Pedagogical University, Poland; *P Piekarz*, Polish Academy of Sciences, Poland; *G Jaglo*, Pedagogical University, Poland; *L Havela*, Charles University, Prague, Czech Republic
Uranium monocarbide, a potential fuel material for the generation IV reactors, is investigated within density functional theory. Its electronic, magnetic, elastic, and phonon properties are analyzed and discussed in terms of spin-orbit interaction and localized versus itinerant behavior of the 5f electrons. We demonstrate that the theoretical electronic structure, elastic constants, phonon dispersions, and their densities of states can reproduce accurately the results of x-ray photoemission and bremsstrahlung isochromat measurements as well as inelastic neutron scattering experiments only when the 5f states experience the spin-orbit interaction and simultaneously remain partially localized [1]. The partial localization of the 5f electrons could be represented by a moderate value of the on-site Coulomb interaction parameter of about 2 eV. The results of the present studies indicate that both strong electron correlations and spin-orbit effects are crucial for realistic theoretical description of the ground-state properties of uranium carbide. This is even more pronounced considering the thermal expansion and thermal conductivity of UC, where for the latter the optical phonon branches may cause a significant contributions [2]. We compare the novel material UC to the experimental data and to the presently used nuclear fuel material, UO₂ oxide. Here our calculations show that considering the exchange and electron correlations effects the generalized gradient approximation was successful in describing the phonon dispersion spectrum, thermal expansion, and heat capacity w.r.t to the recorded data [3]. For both materials the so-called direct method, based on the harmonic and quasi-harmonic approximation, was used [4]. To study the pressure dependence of the phonon frequencies of UO₂ we calculated phonon dispersions for several lattice constants. Our computed phonon spectra demonstrate the opening of a gap between the optical and acoustic modes induced by pressure. Taking into account the phonon contribution to the total free energy of UO₂ its thermal expansion coefficient and heat capacity have been computed from first-principles [3].

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Biomaterial Interfaces Division

Room 12 - Session BI+AS+MI+SA-TuA

Bio from 2D to 3D: Challenges in Fabrication and Characterization & Flash Presentations

Moderators: Lara Gamble, University of Washington, Anna Belu, Medtronic, Inc.

2:20pm BI+AS+MI+SA-TuA-1 Cell-instructive Polymer Matrices for Therapies and Tissue Models, **Carsten Werner**, Leibniz Institute of Polymer Research Dresden and TU Dresden, Deutschland **INVITED**

Sulphated and non-sulphated glycosaminoglycans (GAGs) can be instrumental in biomedical technologies beyond. In particular, incorporation of GAGs into biomaterials has been demonstrated to allow for the biomimetic modulation of growth factor signaling, providing control over therapeutically relevant cell fate decisions in various different settings. In an attempt to systematically explore the related options, we have introduced a rational design strategy for biology-inspired hydrogels based on multi-armed poly(ethylene glycol), GAGs and peptides (1,2,3). The theoretically predicted decoupling of biochemical and mechanical gel properties was confirmed experimentally and applied for implementing GAG-based biofunctionalization schemes to afford cell adhesiveness and morphogen presentation. A number of applications of customized GAG-based materials will be given, including inflammation-modulating wound dressings (3), cryogel particles to support cell replacement in Parkinson's disease (4) and gel matrices to enable tissue and disease *in vitro* models for cancer biology (5,6) and nephrotoxicity studies. In sum, our reported

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approach demonstrates the power of joint theoretical and experimental efforts in creating bioactive materials with specifically and independently controllable characteristics (7).

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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 Agrosience GmbH, Germany; *M Ani*, University of Kaiserslautern, Germany; *K Boonrod*, RLP Agrosience GmbH, Germany; *C Müller-Renno*, University of Kaiserslautern, Germany; *G Krczal-Gehring*, RLP Agrosience 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 biosensors 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.

Lüders et al. (2012). Tomato bushy stunt viruses (TBSV) in nanotechnology investigated by scanning force and scanning electron microscopy. *Colloids Surf. B91*, 154

3:20pm BI+AS+MI+SA-TuA-4 Designing Thermo-responsive Nanocomposites that Provides Multiple Defense Mechanisms against Fouling, *Ya Liu*, University of Pittsburgh; *C Zhang*, *S Kolle*, *J Aizenberg*, Harvard University; *A Balazs*, University of Pittsburgh

We use computational modeling to design synthetic gel-based composite coatings that provide multiple defense mechanism against the fouling of the underlying substrate. The system encompasses rigid posts embedded in a lower critical solution temperature (LCST) thermo-responsive gel, which swells at lower temperatures and collapses at higher temperatures. By developing new dissipative particle dynamics (DPD) simulation that capture the cell-surface interactions, we examine the biofilm growth and structure development on the substrates and pinpoint the parameter space that yields the optimal antifouling behavior for this system. The advantage of our approach relies on physical mechanisms and doesn't have unwanted environmental consequences.

4:20pm BI+AS+MI+SA-TuA-7 3D Ink-jet Printing for Tissue Engineering, *Thomas Boland*, The University of Texas at El Paso **INVITED**

An inkjet application is described, where biologically active ink, which may include drugs and living cells as well as non-active can be deposited alongside scaffolding materials to build two- and three-dimensional constructs for medical treatment. The technology faces several limitations that present interesting engineering opportunities. The nature and scope of the problems will be discussed in the context of the fabrication of microvasculature. The current tissue engineering paradigm is that successfully engineered thick tissues must include vasculature. As biological approaches alone such as growth factors have fallen short of their promises, one may look for an engineering approach to build microvasculature. Layer-by-layer approaches for customized fabrication of cell/scaffold constructs have shown some potential in building complex 3D structures and with the advent of cell printing, one may be able to build precise human microvasculature. Several research projects will be presented. The fabrication of microvasculatures for skin and adipose tissue engineering and current studies to characterize the biology and functionality of these engineered structures will be presented. These data suggests that a combined simultaneous cell and scaffold printing can promote microvasculature formation and improve current tissue engineering technology.

5:00pm BI+AS+MI+SA-TuA-9 Digging for Answers: Challenges in ToF-SIMS Tissue Depth Profiling, *Daniel Graham*, University of Washington, Seattle; *T Angerer*, University of Washington, Seattle, Sweden; *L Gamble*, University of Washington, Seattle

The advent of cluster ion beams for time-of-flight secondary ion mass spectrometry (ToF-SIMS) instrumentation has opened up many opportunities for depth profiling organic samples. Combined with its high lateral resolution imaging capabilities, SIMS can provide 3D imaging information from a wide range of organic materials including cells and tissues. The ability to track chemical changes both across and throughout tissue sections could help identify molecular changes related to targeted drug delivery or disease states in the cellular micro-environment. While there have been many studies showing the utility of ToF-SIMS depth profiling for polymer materials, similar studies with cells and tissues have been limited. This has likely been due to the challenges encountered when working with biological samples. It has been shown that one can depth profile cells as long as the levels of buffer salts and other inorganic components is minimized. Similar work with depth profiling tissues has been limited. Herein we will present our findings on the challenges of depth profiling tissues and discuss ways these challenges may be avoided. Examples will be shown using both single beam argon cluster depth profiling and dual beam depth profiling using Bi³⁺ for analysis and argon clusters for sputtering. In general a significant loss in signal is seen after the first few layers of a tissue depth profile. This could be due to migration of components to the surface, ion beam damage, or ion suppression due to salts. In spite of these issues, tissue depth profiles can be acquired in most cases. The challenge then becomes processing and interpreting these large data sets. Ideas on how to overcome these challenges will be presented.

5:20pm BI+AS+MI+SA-TuA-10 Cryo-SIMS – Metrology of Biological Sample Preparation Methods for Preservation of Cell Ultrastructure and Chemistry, *Paulina Rakowska*, *J Vorng*, *I Gilmore*, National Physical Laboratory, UK

With the potential of high-throughput, high-resolution and high-sensitivity label-free imaging in 3D, secondary ion mass spectrometry imaging methods are, arguably, ones of the most powerful techniques for high-resolution chemical imaging of biological samples. However, there are

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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 **BI+AS+MI+SA-TuA-11 Towards Cryogenic 3D Nano-XRF Imaging of Biological Samples**, *Axel Rosenhahn, S Stuhr, C Rumancev, T Senkbeil, T Gorniak, A von Gundlach, J Reinhardt*, Ruhr-University Bochum, Germany; *Y Yang, P Cloetens*, ESRF, France; *M Grunze*, Karlsruhe Institute of Technology (KIT), Germany; *J Garrevoet, G Falkenberg, W Schröder*, DESY, Germany
Nanoprobe 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 Steinrück*¹, University Erlangen-Nuernberg, 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.

F. Maier, I. Niedermaier, and H.-P. Steinrück, "Perspective: Chemical Reactions in Ionic Liquids Monitored through the Gas (Vacuum)/Liquid Interface", *J.Chem. Phys.* **2017** (in press)

H.-P. Steinrück and P. Wasserscheid, "Ionic Liquids in Catalysis", *Catal. Lett.* **2015**, *145*, 380.

H.-P. Steinrück, "Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions", *Phys. Chem. Chem. Phys.* **2012**, *14*, 2510.

H.-P. Steinrück, "Surface Science goes liquid!", *Surf. Sci.* **2010**, *604*, 481.

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 Troian, S Yngman*, Lund University, Sweden; *H Sezen, M Amati, L Gregoratti*, Elettra-Sincrotrone Trieste, Italy; *A Mikkelsen, R Timm*, Lund University, Sweden

III-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 (SPeM) at the ESCAMicroscopy beamline of the ELETTRA synchrotron, providing a lateral

¹ Medard W. Welch Award Winner

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resolution of about 120 nm, for imaging individual NWs. In addition, we revealed the change in local surface potential across (Ga)InP *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 wurtzite 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.

[1] E. Lind *et al.*, IEEE J. El. Dev. Soc. **3**, 96 (2015).

[2] J. Wallentin *et al.*, Science **339**, 1057 (2013).

[3] R. Timm *et al.*, Appl. Phys. Lett. **99**, 222907 (2011); J. Webb *et al.*, Nano Lett. **15**, 4865 (2015).

[4] M. Hjort *et al.*, ACS Nano **8**, 12346 (2014).

3:20pm SA+AS+HC+SS-TuA-4 Introducing Ionic-Current Detection for X-ray Absorption Spectroscopy in Liquid Cells, Daniela Schoen, Helmholtz-Zentrum Berlin, Germany

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 aqueous solutions 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 adsorbed 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-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 conductive, 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-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 Gassilloud, M Bernard, M Veillerot, CEA/LETI-University Grenoble Alpes, France; J Ablett, 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 Al₂O₃-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 HAXPES 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 TaN/TiTe/Al₂O₃/Ta 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 (Al₂O₃). 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

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2. Waser R, Dittmann R, Staikov G, Szot K. Redox-Based Resistive Switching Memories - Nanoionic Mechanisms, Prospects, and Challenges. *Adv Mater.* 2009 Jul 13;21(25-26):2632–63.

3. Jameson JR, Kamalanathan D. Subquantum conductive-bridge memory. *Appl Phys Lett.* 2016 Feb 1;108(5):053505.

5:40pm SA+AS+HC+SS-TuA-11 Correlation of the Magnetic and Magnetotransport Properties, Electronic and Atomic Structure of Strongly Correlated Complex-oxide Thin Films with the Oxygen Vacancies and Films Thickness, German Rafael Castro, Spanish CRG BM25 Beamline at the ESRF, France; J Rubio Zuazo, Spline Spanish CRG BM25 Beamline at the ESRF, France

Herewith, we present structural, electronic, morphological and magnetotransport properties of thin films of perovskite-manganese oxides (manganites) grown on SrTiO₃(001) by oxygen assisted pulsed laser deposition (PLD) methods, using Hard X-ray Photoelectron Spectroscopy (HAXPES), and Grazing Incidence X-ray diffraction (GIXRD).

Perovskite-manganese oxides exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. La_{1-x}CaxMnO₃-type perovskite-manganese oxides are strongly correlated electron systems and exhibit, in the Ca doping range between 0.15 and 0.5, a ferromagnetic-paramagnetic (FM) phase transition accompanied by a metal-insulator (MI) transition that results in a colossal magneto-resistance behaviour. In bulk La_{0.7}Ca_{0.3}MnO₃ (LCMO), the transition temperature T_{FM}, T_{MI} rises for 33% Ca doping level reaching values close to room temperature. The results shown here are focused on the study of the influence of buried interfaces and the oxygen vacancies on the electric and magnetotransport properties of La_{0.7}Ca_{0.3}MnO₃ thin films grown on SrTiO₃(001)

The growth of these materials in thin film form opens possibilities for magneto-electronic devices applications. The atomic and electronic structures, as well as the oxygen content, are followed simultaneously by GIXRD and HAXPES. Combining GIXRD, HAXPES and transport techniques, we have established a correlation between the electronic, atomic structure

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and magnetic and magnetotransport properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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.

Tuesday Evening Poster Sessions, October 31, 2017

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 $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}/\text{AlN}/\text{GaN}$ 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 $3p_{3/2}$ 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

- [1] P. Risteruci et al., Applied Physics Letters, 104, (2014).
- [2] C. Zborowski et al., Applied Surface Science, (Submitted).
- [3] S. Tougaard, Journal of Electron Spectroscopy and Related Phenomena, 178–179 (2010).
- [4] P. Risterucci et al., Applied Surface Science, 402, (2017).

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.

SA-TuP-3 Hard X-ray Photoelectron Spectroscopy in the Home Laboratory: A Commercially Available System, *Susanna Eriksson, P Palmgren, M Patt, M Heiss, P Baumann, P Zeigermann, T Wiell, K Backlund, C Liljeborg, M Lundqvist, Scienta Omicron*

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 a wide acceptance angle hemispherical electron analyzer, both combined on a simple to use vacuum system. The base system can easily be 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 ERIC, 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 on-Evaporable Getter and Sputter Ion Pump combination pumps 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

Applied Surface Science Division

Room 13 - Session AS+BI+MI+NS+SA+SS-WeM

Beyond Traditional Surface Analysis: Pushing the Limits

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

8:00am AS+BI+MI+NS+SA+SS-WeM-1 Photolysis of Pyruvic Acid in Aqueous Solution as a Source of Aqueous Secondary Organic Aerosol, Yao 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., dimethyltartaric acid), and water clusters (i.e., $(\text{H}_2\text{O})_n\text{H}^+$, $(\text{H}_2\text{O})_n\text{OH}^-$) with submicrometer spatial resolution. Spectral principal component analysis is used to determine similarities and differences among various photochemical aging samples. SIMS three-dimensional 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 surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

8:20am AS+BI+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 photocatalysis, 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 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 (MAGCIS) profiles were recorded using 8 keV Ar₁₀₀₀⁺ and 8 keV Ar₁₅₀⁺ for SrTiO₃ and HfO₂ respectively. For HfO₂ the optimum results were found when the MAGCIS ion beam was incident upon the sample at a glancing angle. These MAGCIS 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 of Ti in SrTiO₃ and Hf and HfO₂. 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 Ar₁₀₀₀⁺ 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.

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

INVITED

Secondary ion mass spectrometry (SIMS), as the oldest MSI techniques, gained popularity for analysis of biological samples due to its ability to obtain chemical and spatial information at unmatched lateral resolutions. 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, SIMS has been pushing the boundaries 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 ((Meta) 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.

9:20am AS+BI+MI+NS+SA+SS-WeM-5 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.

9:40am AS+BI+MI+NS+SA+SS-WeM-6 Fragmentation and Backscattering of Large Ar_n⁺ Clusters as a Probe of Polymer Glass Transition, C Poleunis, 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_n⁺ 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 Ar₂⁺ to the sum of Ar_n⁺ 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_n⁺ clusters are studied as a function of temperature for a series of thermoplastic polymers: high

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molecular weight polydisperse polyisobutylene and polybutadiene, polystyrene (Standard; $M_w = 4000$) and polymethyl methacrylate (Standards; $M_w = 2000$ and 150000). For all these polymers, our results show a transition of the intensity ratio $Ar_2^+/(Ar_2^++Ar_3^+)$ 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 (T_g) 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 T_g 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.

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11:00am **AS+BI+MI+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 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 Bi₃⁺⁺ species [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_n) 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.

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11:40am **AS+BI+MI+NS+SA+SS-WeM-12 Evaluating the Benefits of Cs Cluster Analysis in ToF-SIMS and Cs/Xe Co-sputtering for Depth Profiling Layered Thin Films, James Ohlhausen, P Vianco, M Brumbach, R Chow, Sandia National Laboratories**

Depth profiling with Cs to create MCs⁺ clusters can produce semi-quantitative results by greatly reducing the matrix effects observed in common M⁺ analysis. Additionally, alkali metal clusters enhance negative ion detection in the form of positive Cs clusters, such as MCs⁺ and MCs₂⁺. In his review article, Wittmaack¹ discussed the many ways that Cs is used in SIMS analyses to provide this enhancement which includes using Cs as the sputtering species and/or analytical probe and using directed Cs vapor. Unfortunately, high Cs surface concentrations can lead to suppression of Cs cluster formation. Xenon and Cs can be co-sputtered in a ToF-SIMS system to adjust the relative amounts of Cs and Xe in the co-sputtered beam to control Cs surface concentration and optimize Cs cluster formation². Cs/Xe co-sputtered depth profiling has been shown to work well in materials systems such as Au thin film on Si³ and Pd-Rh thin film⁴.

The present paper discusses the use of Cs/Xe co-sputtering to investigate an Au/Pd/Ni electroplated layered system. Gold and to some extent Pd have low positive ionization yields, so typical ToF-SIMS data from these metals can be difficult to interpret. However, Cs/Xe co-sputtering has been found to generate high yield MCs⁺ clusters in Au and Pd, thus enabling this analysis. This Au/Pd/Ni metal stack were analyzed in a pristine (as received) condition, after accelerated aging and after exposure to a (very high temperature) solder reflow process. The elemental and molecular sensitivities as well as quantitative results stemming from this analysis will be investigated. The manner whereby these results support the use of Au/Pd/Ni stack in an engineering application will be shown. In particular, interlayer diffusion, trace contaminants and interfacial contamination will be examined. Comparisons will be made to Auger and XRF to assess quantitation and sensitivity and to illustrate the advantage of this SIMS technique.

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Sandia National Laboratories is a multimission 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-NA-0003525.

12:00pm **AS+BI+MI+NS+SA+SS-WeM-13 Real-Time Monitoring Electrochemical Reaction Intermediates using In Situ Time-of-Flight Secondary Ion Mass Spectrometry, Jun-Gang Wang, East China University of Science and Technology; Pacific Northwest National Laboratory (PNNL), China; Y Zhang, X Yu, Z Zhu, PNNL**

In situ monitoring of electrochemical reactions is traditionally performed by cyclic voltammetry[1], plasmonic spectroelectrochemistry[2, 3], and surface probing techniques such as scanning electrochemical microscopy and scanning ion conductive microscope.[4] However, it has been extremely difficult to obtain direct molecular evidence of the electrochemical reaction intermediates using these traditional techniques. Thus, the debate of reaction mechanisms has long been an issue. Recently, mass spectrometric techniques have been coupled with electrochemistry to provide the molecular information of intermediates of redox reactions.[5] The advantage of mass spectrometric techniques is that capture of molecular ions can provide direct molecular information of key chemical species, such as reaction intermediates. A novel approach, based on coupling of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrochemistry has been developed in Pacific Northwest National Laboratory and it has been used for in situ analysis of reaction intermediates in electro-oxidation of ascorbic acid at the electrode-electrolyte interface.[6] Herein, the electrochemical oxidation of acetaminophen was chosen as a model system, which simulated the function of oxidase enzymes cytochrome P-450 to catalyze the oxidation of acetaminophen.[7] This reaction was real-time monitored using in situ ToF-SIMS. The highly reactive N-acetyl-p-benzoquinone-imine (NAPQI) was captured. The NAPQI subsequently conjugated with glutathione and cysteine was molecularly confirmed. We demonstrated the proof of principle for the use of ToF-SIMS for real-time monitoring of electrochemical reaction with high chemical specificity. Our results

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

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Magnetic Interfaces and Nanostructures Division

Room 11 - Session MI+SA-WeM

Controlling 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 [1-9]. Strong magnetoelectric 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 $f200\mu\text{m} \times 1\mu\text{m}$ or $l_0/600$ in size, -18dB gain, self-biased operation and $1\sim 2\%$ 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 voltage tunable inductance of 50%~150%. At the same time, I will also demonstrate other voltage tunable multiferroic devices, including tunable isolating bandpass filters, tunable bandstop filters, tunable phase shifters, etc. These novel integrated multiferroic devices show great promise for applications in compact, lightweight and power efficient sensing, power, RF, microwave and mm-wave integrated electronics.

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9:20am MI+SA-WeM-5 Controlling Spin Selectivity in Photoinduced Charge Transfer through Patterned DNA Microarrays, *John Abendroth*¹, *N Nakatsuka*, *M Ye*, *D Steiner*, 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.

9:40am MI+SA-WeM-6 Anomaly in Electric Transport Behaviour of Fe₃O₄ Thin Films, *Murtaza Bohra*, Mahindra Ecole Centrale, India

Nanocrystalline Fe₃O₄ thin films were grown by adopting two different reduction approaches (1) vacuum annealing (2) wet H₂ annealing. While vacuum annealed films shows Verwey transition with lower resistivity compared to the bulk Fe₃O₄, the same are not observed in electric transport properties of wet H₂ annealed films. However, this transition was clearly seen in the temperature dependence of magnetization of both sets of Fe₃O₄ thin films. This seems to indicate that the both electric transport and magnetization are independent processes; it's just coincidence to happen at same place of Verwey transition at 120 K in Fe₃O₄. Different electric transport properties in both reductions treated Fe₃O₄ films could be ascribed to different grain sizes/grain boundary volumes, inhomogeneities and presence of residual atomic-H at grain boundaries emanating from complex reductions treatments.

11:00am MI+SA-WeM-10 Intrinsic Interfacial Phenomena and Spin Structure in Nano and Heterostructures, *Carlos Vaz*, Paul Scherrer Institut, Switzerland **INVITED**

One fundamental route towards the control of the electronic properties of materials is via modulation of the charge carrier density, either through chemical, ionic, or electrostatic doping. The latter process relies on charge screening effects at the interface between a gate dielectric and a channel layer, and forms the basis of important technological applications, such as field effect devices. A more recent extension of this concept employs a ferroelectric gate dielectric in combination with correlated materials to form switchable, non-volatile ferroelectric field effect devices, or artificial multiferroic heterostructures relying on interfacial modulations of the magnetic properties of the channel layer [1]. A particularly striking manifestation of the latter has been found in ferroelectric/ferromagnetic mixed valency manganite heterostructures, where control of the ground state of a 10 unit cells La_{0.8}Sr_{0.2}MnO₃ film (LSMO) in contact with a ferroelectric PZT layer leads to a spin reconstruction in the LSMO that is intrinsic to the PZT/LSMO interface, as a consequence of the modulation in the charge density [2]. In this contribution I discuss recent results aiming at resolving the magnetic configuration of the interfacial spin reconstruction in the LSMO using soft x-rays as a localised probe of the electronic and magnetic structure at the interface. In particular, I show that resonant x-ray magnetic reflectivity can probe deeply buried interfaces with high sensitivity. Changes in the reflectivity spectra are observed upon switching of the ferroelectric polarisation and reflect directly the changes in the spin structure at the interface. The results of these studies underline the unique strengths of synchrotron x-ray light to address fundamental and practical issues in a wide range of physical systems [3].

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¹ Falicov Student Award Finalist

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11:40am **MI+SA-WeM-12 Enantiomer-dependent Spin Orientation in Photoelectron Transmission through Heptahelicene Molecules**, *Matthias Kettner, D Nürenberg*, University of Münster, Germany; *J Seibel*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *H Zacharias*, University of Münster, Germany; *K 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.

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12:00pm **MI+SA-WeM-13 Spin-selective Electron Transmission through Self-Assembled Layers of PNA**, *Paul Möllers, M Kettner, D Nürenberg*, Westfälische Wilhelms-Universität Münster, Germany; *F Tassinari, T Markus*, Weizmann Institute of Science, Israel; *C Achim*, Carnegie Mellon University; *R Naaman*, Weizmann Institute of Science, Israel; *H Zacharias*, Westfälische Wilhelms-Universität Münster, Germany

The yield of electrons transmitted through chiral molecules can depend on the electron's spin; chiral molecules can therefore act as spin filters. This effect is referred to as chirality-induced spin selectivity (CISS). Previous experiments have e.g. been performed with monolayers of double-stranded DNA adsorbed on gold [1] and silicon [2] substrates. In this contribution, we present results of our spin-resolved photoemission experiments performed at room temperature. The samples consist of self-assembled monolayers of helical molecules – various types of double-stranded peptide nucleic acid (PNA) – on polycrystalline gold surfaces. The samples are irradiated by a laser at $\lambda = 213\text{nm}$ to generate photoelectrons from the gold substrate which are then transmitted through the adsorbed monolayer. Subsequently, the electrons are analyzed by a Mott polarimeter. We found longitudinal spin polarizations of $\sim 6\%$ for PNA and $+25\%$ for γ -PNA. The results indicate that the adsorbed molecules act as a spin filter.

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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-Nuernberg, Germany, Kristina Edström, Uppsala University, Sweden

8:00am **SA+2D+AC+MI-WeM-1 Studies of Surfaces and Catalysis in real time with X-ray Free Electron Laser**, *Anders Nilsson*, Stockholm University, Sweden **INVITED**

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 Ghiringhelli*, 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 L₃ 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.

[1] Y. Y. Peng, G. Dellea, M. Minola, M. Conni, A. Amorese, D. Di Castro, G. M. De Luca, K. Kummer, M. Salluzzo, X. Sun, X. J. Zhou, G. Balestrino, M. Le Tacon, B. Keimer, L. Braicovich, N. B. Brookes and G. Ghiringhelli, [<https://arxiv.org/abs/1609.05405>]

[2] H. Miao, J. Lorenzana, G. Seibold, Y.Y. Peng, A. Amorese, F. Yakhov-Harris, K. Kummer, N. B. Brookes, R. M. Konik, V. Thampy, G. D. Gu, G. Ghiringhelli, L. Braicovich, M. P. M. Dean, [<https://arxiv.org/abs/1701.00022>]

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 LaTiO₃ layers in (LaTiO₃)_n/(LaAlO₃)_s superlattices undergoing a transition from Ti³⁺ to Ti⁴⁺ oxidation state upon reducing *n* and thickness as well as temperature-driven metal-insulator transitions in thin films of CaVO₃.

(LaTiO₃)_n/(LaAlO₃)_s superlattices (SL) composed of a band-insulator (LaAlO₃) and a Mott-insulator (LaTiO₃) 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

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nominal Ti^{3+} ($3d^1$, $n=10$ u.c.) for bulk $LaTiO_3$ to an almost pure Ti^{4+} ($3d^0$, $n=2$ 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_6 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 $3d^1 \rightarrow 3d^0$ 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 spectroscopies 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^2 -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^2 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, spectroscopic 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_3^+ and Ar_n^+ 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.

[1] Nees, R. et al., *Biointerphases*, 2016. 11(2): p. 02A305.

[2] Pelster, A., et al., *Analytical Chemistry*, 2016. 88(19): p. 9638-9646.

[3] Pelster, A., et al., *Biointerphases*, 2016. 11(4): p 041001.

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 Nanoelectronic and Energy Applications**, *Jean-Paul Barnes, A Priebe, G Goret, I Mouton, A Grenier, G Audoit, P Bleuget, Y Mazel, E Nolot*, Univ. Grenoble Alpes, CEA, LETI, France; *S Legendre, A Tempez*, Horiba France S.a.s., France; *R Estivill, M Juhel*, STMicroelectronics, France; *S Duguay, 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 curtaining. These may be identified and corrected by analyzing the sample beforehand by X-ray CNT in a 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].

[1] A. Priebe et al. *Ultramicroscopy*. 173 (2017):10-13.[2] A. Grenier et al *APL* 106, 213102 (2015). [3] A. Tempez et al., *J. Vac. Sci. Technol. B* (2016) 34

4:20pm **AS+2D+NS+SA-WeA-7 Insights into Corrosion and Radiation Damage Processes Through 2D and 3D Imaging at the Nanoscale**, *Karen Kruska, D Schreiber, D Edwards, Z Zhai, M Olszta, I Arslan, M Conroy, C Wang, R Kurtz, S Bruemmer*, Pacific Northwest National Laboratory **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 Gay*, CEA-Leti, France; *M Frégnaux*, 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

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as MoS₂, WSe₂, ...) has amplified the need for advanced analytical diagnostics. One of the main issues to tackle are directly related to the atomically-thin character of the samples, first concerning the low elemental concentrations and second, the invasive character of most of the characterization techniques implemented. As a photon-probe technique, XPS has a key role to play in the analysis of TMDs but highly sensitive and versatile microscopic capabilities are needed: this is because the physics of TMDs, notably the indirect-to-direct band gap transition in the monolayer limit, requires spatially-resolved information not only on the chemical composition but also on the electronic band structure. Short analysis times are required because a screening of these properties depending on processing conditions (at the material or the device level) is needed. PEEM-based instruments are the only class of XPS microscopes able to offer both type of analysis. In this presentation, we will review recent studies of 2D materials using XPEEM for chemical imaging and kPEEM for band structure imaging, with a particular emphasis on instrumental requirements (excitation source, transmission and detection) and post-processing of the 3D spectroscopic image data sets. The examples will range from graphene doping [1] and cleaning [2], to single layer MoS₂ [3-4], including also novel materials and 2D heterostructures.

This work was performed at the Platform For Nano-Characterization of CEA-MINATEC.

- [1] H. Kim, O. Renault *et al.*, *Appl. Phys. Lett.* **105**, 011605 (2014).
- [2] M. Frégnaux, O. Renault *et al.*, *Surf. Interface Anal.* **2016**, 48, 465-469.
- [3] D. Ferrah, O. Renault *et al.*, *Surf. Interface Anal.* **2016**, 48, 451-455.
- [4] H. Kim, M. Frégnaux, A. Kis, O. Renault, *et al.*, *Phys. Rev. B* **34**, 081401 (R) (2016).

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 resulting SAMs. Our results¹ 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 structural domains. Importantly, this pronounced difference in 2D ordering is observed despite the approximately 300 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 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

[1] A. Krzykawska, J. Ossowski, T. Zaba and P. Cyganik, *Chem Comm* **2017** accepted

5:40pm **AS+2D+NS+SA-WeA-11 2-D and 3-D Characterization of Functionalized Nanostructured Carbons**, *Chilan Ngo, D Diercks, M Strand, M Dzara, J Hagen, S Pylypenko*, Colorado School of Mines

Low cost, versatility, and a broad range of properties make carbon a widely studied material with numerous practical applications. Functionalization/doping with heteroatoms is an effective method to tailor the composition and structure of carbon, in order to adjust its properties for various applications. Significant efforts have been dedicated to elucidation of the composition, structure and properties of doped carbon materials, however atomic scale visualization of high-surface area carbons in 3-D has not been achieved. Here, by utilizing a combination of techniques, we focus on understanding the 2-D and 3-D distribution of nitrogen and iron dopants in high-surface area carbons. Information on surface composition evaluated using X-ray photoelectron spectroscopy (XPS) is complemented by 2-D bulk measurements using energy dispersive X-ray spectroscopy (EDS) through transmission electron microscopy (TEM). 3-D distribution of dopants is studied using atom probe tomography (APT), providing novel insight into the properties of high-surface area carbon materials. This type of investigation necessitated the fabrication of a diverse set of materials with defined shape and morphology, along with variation in the distribution of nitrogen and iron species relative to each other. Nitrogen-doped carbon nanospheres (NCs) were prepared by hydrothermal treatment of resorcinol, formaldehyde, and ethylenediamine, followed by pyrolyzation under flowing nitrogen, producing materials with different dopant concentrations and varied relative distribution of nitrogen functionalities. Iron- and nitrogen-doped nanospheres (FeNCs) were prepared by two routes. For the first set of materials, addition of an iron-containing precursor to the NC synthesis was done prior to hydrothermal treatment, to incorporate Fe throughout the bulk of the nanosphere. The second set is expected to deposit iron only on the surface of the carbon, and is prepared by addition of the iron precursor after the NC pyrolysis, followed by a second pyrolysis. A dual-beam focused-ion beam scanning electron microscope (FIB/SEM) was used to isolate nanospheres into a workable APT tip. Combination of 2-D and 3-D analysis are expected to further the understanding of N-doped carbon materials and N-containing Pt-group metal free catalysts employed in a variety of important catalytic reactions. This work also serves as a foundation to prepare model high-surface area materials that are compatible with *in situ* liquid and electrochemistry TEM techniques, to allow further investigations of these catalytically active materials under conditions relevant to their applications.

6:00pm **AS+2D+NS+SA-WeA-12 Characterization of Natural Photonic Crystals in Glitterwing (*Chalcopteryx rutilans*) Dragonfly Wings using 3D TOF-SIMS**, *Ashley Ellsworth, D Carr, G Fisher*, Physical Electronics; *W Valeriano, R de Andrade, J Vasco, E da Silva, A Machado, P Guimarães, W Rodrigues*, Universidade Federal de Minas Gerais, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) dragonfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for dragonflies with regard to sexual recognition, mating, and territorial behavior. The source of the varying colors was determined by Valeriano [1] using electron microscopy and optical reflectance to analyze the internal microstructures. SEM and TEM images revealed that the iridescent wings have multiple alternating layers with different electronic densities. The variation of the local color was related to the number and thickness of the layers which varied across the wing. The colors span the visible spectrum with red, blue, and yellow/green regions on the wings. The experimental reflectance was calculated and fitted through the transfer matrix method for the structure obtained from the electron microscopy images. Measurement of the thickness and number of layers is readily achievable by electron microscopy, however it is unable to characterize the chemistry of the different layers giving rise to these natural photonic crystals.

TOF-SIMS is a well-established technique for analyzing the elemental and molecular chemistry of surfaces. TOF-SIMS can now be used to probe the 3D structure and chemistry of a wide variety of organic and inorganic materials, both synthetic and naturally occurring, due to the advent of cluster ion beams such as C₆₀⁺ and large cluster Ar_n⁺. We will present results of 3D TOF-SIMS analyses for both transparent and colored wings to correlate with the electron microscopy and optical results to further the understanding of these natural photonic crystals.

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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 Myochi, S Takahashi, N Todoroki, Toshimasa Wadayama*, 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_{1.6nm}/Co_{0.4nm}/Pt_{3.6nm}/Co_{0.4nm}/Pt(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 linear sweep voltammetry (LSV) were conducted in N₂-purged and O₂-saturated 0.1M HClO₄ in the glove-box. To discuss EC stability, square-wave potential cycling between 0.6(3s) ~ 1.0(3s) V vs. RHE was applied.

ORR properties (initial activity & durability) of the samples closely correlate with the Co (Co-N) thickness underlying the topmost Pt layer. For example, the activity enhancement factor for the U_{Co_16A} is highest (13-fold vs. Pt(111)) for the Pt/Co/Pt(111). ORR activity enhancement well corresponds to in-plane lattice distance estimated by the XRD. The results suggest that the ORR enhancements are determined by compressive surface strains that work on the topmost Pt(111) layers induced by underlying Co (Co-N) layers.

We wish to acknowledge the NEDO and JSPS.

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2:40pm **HC+SA+SS-WeA-2 The Mechanism of Oxygen Induced p(2×3) Reconstruction on Mo(112)**, *Teng Ma*, Shenyang Agricultural University, PR China

Oxygen induced reconstruction and oxidation of Mo(112) surface has shown various surface structures in model catalysis and surface studies. Because of its complexity, the p(2 × 3) reconstruction has been modeled as several patterns and its formation mechanism was not well clarified. In this report, a critical precursor of forming p(2 × 3) reconstruction has been observed by using STM, XPS and HREELS methods. For the Mo(112) surface exposed to 5.0×10⁻⁸ mbar O₂, the formation of the p(2×3) reconstruction is a process of two consecutive steps, during which the clean metallic surface experience the initial oxidation to form dispersed oxide particles at nanoscale, and then reduction and structural rearrangement of molybdenum oxides to the ordered nanostructures. The features of surface structures are also temperature dependent, a mixture of dispersed nanoparticles of molybdenum oxide and one-dimensional nanostructures occurs after O₂ dose at 605 K, while two-dimensional nanostructures or the

p(2×3) reconstruction occurs until above 710 K. Our results would give a good explanation about some hurdled questions about the appearance of LEED streaky points and antidomain dislocations in the STM images of the p(2 × 3) reconstruction.

3:00pm **HC+SA+SS-WeA-3 Gas-Liquid Scattering Studies of Atmospheric Reactions at the Surfaces of Sea-Spray Mimics**, *M Shalowski, J Gord*, University of Wisconsin - Madison; *S Staudt*, University of Wisconsin-Madison; *S Quinn, T Bertram*, University of Wisconsin - Madison; *Gilbert Nathanson*, University of Wisconsin-Madison

INVITED

Heterogeneous reactions between atmospheric gases and sea-spray aerosols are fascinating examples of complex interfacial processes involving water, ions, and surface-active molecules. These reactions are also important because of the controlling role they play in regulating pollution and greenhouse gases in the troposphere. Of particular interest is the atmospheric molecule N₂O₅, created indirectly by fossil fuel burning. During the day, N₂O₅ is photolyzed to NO₂ and NO₃, ultimately producing O₃ and then OH· radicals that destroy CH₄. During the night, N₂O₅ can be removed by dissolving into sea-spray aerosols near coastal regions. This dissolution is followed by rapid hydrolysis to HNO₃ or reaction with Cl⁻ to produce ClNO₂, a gas that potentially supplies reactive Cl atoms and returns half of the NO₂ to the atmosphere. The fate of N₂O₅ upon collision with an aerosol droplet is enormously difficult to predict because the droplets are chemically diverse and often possess an outer layer of lipid-like organic molecules. Such surface-active species can inhibit or even enhance uptake and reactivity by orders of magnitude.

We have implemented gas-liquid scattering experiments to investigate the dynamics of these interfacial N₂O₅ reactions. By directing a well-defined beam of N₂O₅ at a stream of salty water emerging from a liquid microjet in vacuum, we can track the uptake and reactivity of N₂O₅ with seawater and sea-spray mimics. We have also used similar experiments involving liquid glycerol to explore the ability of cationic and zwitterionic surfactants to increase ion concentrations of Br⁻ or Cl⁻ at the surface and to stabilize reaction intermediates created by N₂O₅. These studies provide insight into interfacial ionization and bimolecular reactions at the surfaces of complex liquids found in the atmosphere.

4:20pm **HC+SA+SS-WeA-7 In-situ Investigation of Methane Activation on MO_x/CeO₂ (111) Surfaces {M=Co, Ni and Cu} using Ambient-Pressure XPS**, *J Rodriguez, Zongyuan Liu*, Brookhaven National Laboratory

Natural gas has transformed the energy landscape of this nation and has fast become a cheap and abundant fuel stock. Methane is the primary component of natural gas but is difficult to convert it to upgraded fuels or chemicals due to the strong C-H bond in methane (104 kcal/mol). This challenge constitutes one of the most difficult problems in heterogeneous catalysis. We have discovered a catalyst with small Ni nanoparticles supported on ceria that has shown promising activity for both methane activation and dry reforming of methane. Then we expanded the study to other transition metals (Co and Cu) supported on ceria in order to rationalize the structure-reactivity relationships for methane activation. Due to the chemically inert nature of methane, the experiment needs to be conducted at elevated pressure via the utilization of Ambient Pressure of XPS. Nanoparticles or clusters of Co and Cu were deposited onto the well-defined CeO₂(111) surface. Strong metal-oxide interactions were found upon annealing the deposited surfaces to 700 K, leading to the generation of MO_x. In-situ AP-XPS showed that the CoO_x/CeO₂(111) interacted strongly with 50 mTorr of methane, resulting in the formation of Co/CeO_x(111), while no obvious changes were observed on the CuO_x/CeO₂(111) surface (figure 1). By comparing it with the NiO_x/CeO₂(111) surface, it can be found that the methane activation on these MO_x/CeO₂ (111) surfaces follow the order: Co > Ni > Cu. The methane dry reforming activity was also investigated on the CoO_x/CeO₂(111) surface by sequentially adding another 50 mTorr of CO₂ into the system. The slight reoxidation of the ceria surface indicates the participation of CO₂ in the catalytic cycle by the following steps: CH₄(g) → CH_{4-x}(a) + H(a) with x=1-4; CO₂(g) → CO(a) + O(a); C(a) + O(a) → CO(g); H(a) + H(a) → H₂(g).

4:40pm **HC+SA+SS-WeA-8 Ambient Pressure XPS Study of Catalytic Conversion of Carbon Dioxide by CuO_x Nanoparticles Photodeposited on TiO₂ Nanoparticles**, *Djawhar Ferrah, R Galhenaga, J Bruce, A Babore, J Hemminger*, University California, Irvine

The chemical conversion of carbon dioxide to useful products has attracted great interest both from a scientific and industrial perspective. It is widely known that Cu is active for the catalytic hydrogenation of CO₂. However, the detailed structure and oxidation state of the active site is not well understood. Recently, Cu nanostructures were reported to be a promising

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catalyst for hydrogenation of CO₂. 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 (Cu⁰, Cu^I, Cu^{II}, and Cu^{III}), CuO_x-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 reactant adsorption and activation at defects and dangling bonds.

In this study, we investigated the reaction mechanisms in carbon dioxide conversion with CuO_x 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 CuO_x 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 HC+SA+SS-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 steps 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 HC+SA+SS-WeA-10 Structural Consequences of High Oxygen Coverages on Rh(111), Rachael Farber^{1,2}, M Turano, D Killelea, Loyola University Chicago

Partial oxidations of small molecules over metal surfaces are central to many heterogeneously 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 adsorbed below the surface of the metal.

5:40pm HC+SA+SS-WeA-11 Reactivity and Electronic Properties of Supported Metal Oxide and Sulfide Clusters, Michael White, Brookhaven National Laboratory; X Meng, K Goodman, Stony Brook University; P Liu, Brookhaven National Laboratory

INVITED

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 modified at the atomic level. Here, we use mass-selected cluster deposition to prepare model "inverse" catalysts comprised of small metal oxide (M_xO_y; M = Ti, Nb, Mo, Ce, W) and sulfide (M_xS_y; 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 WGS 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 dipoles for sub-stoichiometric and reducible oxides (Ti, Nb). Temperature programmed reaction (TPR) experiments show that the Ti_xO_y and Nb_xO_y clusters promote water dissociation on Cu(111), with the "reduced" Ti_xO_y clusters being more active, while both stoichiometric and reduced Nb_xO_y 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 Ti_nO_{2n} (n = 3, 4, 5) clusters on Cu(111) are active for the WGS reaction through the observation of reaction-induced O-vacancy formation (Ti³⁺ 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 Mo₆S₈ 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 Mo₆S₈ 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.

¹ Morton S. Traum Award Finalist

² National Student Award Finalist

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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, 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.

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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

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 (XPS^{4,5}, XAS^{3,6}) 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 setups⁷. 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

ES, 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.

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3:20pm **SA+AS+HC+SS-WeA-4 A 3D Printed Liquid Cell for Soft X-ray Absorption Spectroscopy**, *Tom Regier*, *T Boyko*, *J Dynes*, Canadian Light Source, Inc., Canada; *Z Arthur*, Canadian Light Source, Inc.; *M Banis*, University of Western Ontario, Canada

Research methods that enable operando studies on energy materials are an important tool for the rational design of materials for renewable energy and carbon neutral technologies. Of particular value is the ability to observe the change in configuration of the 3d orbitals in transition metal based catalysts. Using the excitation of 2p electrons into vacant 3d orbitals, synchrotron based L-edge measurements allow for clear observation of chemical state and co-ordination geometry information from the first row transition elements. Challenges related to the operating in-situ flow cells in soft x-ray beamline endstations have been overcome and operando measurements are now possible at several facilities.

We report on the design of a 3D printed liquid flow cell with built-in electrodes for operando measurements of the transition metal L-edges. The disposable cells can be quickly customized for specific experiments and can be pre-ordered for lab-based characterization before attempting synchrotron measurements. Beamline instrumentation allows for highly sensitive fluorescence yield measurements with 10 micron spatial resolution or 1 minute time resolution.

4:20pm **SA+AS+HC+SS-WeA-7 In Operando Quantification of Valence Changes in Memristive Devices**, *R Dittmann*, *Christoph Baeumer*, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany; *D Cooper*, Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France; *C Schmitz*, *S Menzel*, *C Schneider*, *R Waser*, Peter Gruenberg 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 materials^{1,2}. Direct observation and quantification of the switching mechanism itself, however, remain 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 limiting PEEM investigations of memristive 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.

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5:00pm **SA+AS+HC+SS-WeA-9 Magnetic Skyrmions in Ultrathin Magnetic Films and Nanostructures**, *Jan Vogel*, Institut Néel, CNRS/UGA, Grenoble, France; *O Boulle*, R Juge, SPINTEC, CNRS/CEA/UGA, Grenoble, France; *D Chaves*, S Pizzini, Institut Néel, CNRS/UGA, Grenoble, France; *S Je*, G Gaudin, SPINTEC, CNRS/CEA/UGA, Grenoble, France; *T Mentès*, A Locatelli, Elettra-Sincrotrone Trieste, Italy; *M Foerster*, L Aballe, ALBA Synchrotron Light Facility, Spain

INVITED

Magnetic skyrmions are chiral spin structures with a whirling spin configuration. Their topological properties, small size and sensitivity to small current pulses have opened a new paradigm for the manipulation of magnetization at the nanoscale. Chiral skyrmion were first experimentally observed in bulk materials [1] and in epitaxial ultrathin films [2], under a strong external magnetic field or at low temperature. More recently, it was predicted that they can also be created in thin magnetic films in stacks with structural inversion asymmetry [3]. We have used high lateral resolution PhotoEmission Electron Microscopy combined with X-ray Magnetic Circular Dichroism (XMCD-PEEM) to show that skyrmions with a size around 150 nm can indeed be stabilized at room temperature and without external magnetic field, in nanostructures of Pt/Co/MgO with a Co thickness of 1 nm [4]. The high sensitivity of the technique allows measuring very thin Co layers buried under protecting cover layers. The vectorial information obtained by rotating the sample with respect to the incoming x-ray direction allowed us obtaining information on the 3-dimensional spin structure of the skyrmions, directly showing the chiral spin configuration with left-handed chirality.

We investigated the dependence of the skyrmion size on an applied magnetic field, revealing that already a moderate field of 4 mT can reduce the skyrmion diameter to a size of 70 nm. We also studied the motion of skyrmions in micron-wide strips of Pt/Co/MgO induced by current pulses. The results show that skyrmions can be moved with moderate current pulses with current densities of some 10^{11} A/m², leading to velocities of several tens of m/s.

Our measurements show that synchrotron-based magnetic imaging using PEEM is very powerful for studying the static and dynamic properties of skyrmions in ultrathin magnetic films.

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5:40pm **SA+AS+HC+SS-WeA-11 O₂ Pressure Dependence of SiO₂/Si Interfacial Oxidation Rate Studied by Real-time Photoelectron Spectroscopy**, *Shuichi Ogawa*, Tohoku University, Japan; *A Yoshigoe*, JAEA, Japan; *S Ishidzuka*, National Institute for of Technology, Akita College, Japan; *Y Takakuwa*, Tohoku University, Japan

Thermal oxidation of Si surfaces under the non-equilibrium conditions were used to form a high-quality Si oxide films and/or enlarge the oxidation rate. For example, rapid thermal oxidation (RTO) is performed under the raising the temperature, and then thick oxide can be formed without preventing the dopant diffusions[1]. In addition, the oxidation rate of RTO process is faster than that of constant temperature oxidation (CTO) though the highest temperature of RTO is as same as that of CTO[2]. Based on these knowledges, it is predicted that the oxidation rate at the SiO₂/Si interface can be quickened even by increase of the O₂ pressure. In this study, the increased O₂ pressure dependence of the interface oxidation rate which proceeds contentiously after Si(001) surface oxidation was investigated using real-time photoelectron spectroscopy.

The oxidation experiment was performed using the surface reaction analysis apparatus placed at the BL23SU of SPring-8, Japan. A clean Boron doped p-type Si(001)2x1 surfaces were oxidized at 400°C under the O₂ pressure of 3.2x10⁻⁵ Pa. When clean surfaces were completely covered by the Si oxide, the O₂ pressure was elevated to P_{O₂(int)} in order to enhance the interfacial oxidation. The P_{O₂(int)} was changed between 6.4x10⁻⁵ Pa to 3.2x10⁻³ Pa. O 1s and Si 2p spectra were measured repeatedly during the oxidation. The time evolution of O 1s photoelectron intensity (I_{O1s}) was used for investigation of the oxidation rate.

From the I_{O1s}, we can estimate the completion of surface oxidation as 3200 s. An O₂ pressure was increased up to 1.5x10⁻³ Pa at this time, and then the

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 O₂ 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 O₂ 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 O₂ diffusion. To explain the kinetics, we propose the new interface oxidation model named "Unified Si oxidation model mediated by point defects"[3].

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6:00pm **SA+AS+HC+SS-WeA-12 Highly Time-resolved Insights into the Sputter Deposition of Metal Electrodes on Polymer Thin Films for Organic Electronics**, *Franziska Löhner*, V Körstgens, Technische Universität München, Germany; *M Schwartzkopf*, Deutsches Elektronensynchrotron DESY, Germany; *A Hinz*, O Polonskyi, T Strunskus, F Faupel, Christian-Albrechts-Universität zu Kiel, Germany; *S Roth*, Deutsches Elektronensynchrotron DESY, Germany; *P Müller-Buschbaum*, Technische Universität München, Germany

With their easy processability, high flexibility and tuneable optical properties, organic electronics (OE) offer a wide range of potential applications. Especially photoactive polymers have received attention in recent years as candidates for organic photovoltaics (OPV) and light emitting diodes (OLEDs). Although based on organic materials, their electrodes are typically made from metals due to their unrivaled electronic conductivity. Thus, polymer-metal interfaces are inherently present in most OE devices and have a major influence on their behavior. Understanding the growth mechanisms of metal contacts on polymer thin films plays a crucial role in identifying potential ways to enhance the device performance. We investigate the morphological changes happening at the metal-polymer interface during the sputter deposition of metal contacts onto photoactive polymer films via in-situ grazing incidence small and wide angle x-ray scattering (GISAXS/GIWAXS) [1]. These techniques allow insights into the structural evolution of the metal on the organic film, which depends on various parameters such as the deposition rate or the film morphology. Making use of the brilliant synchrotron light source Petra III at DESY [2], we can study the deposition behavior of the metal on the polymer film with outstandingly high spatial and temporal resolution. The acquired large data sequences are tracked in real-time and further analyzed using the fast data reduction software DPDAK [3]. The final film morphology is characterized via scanning electron microscopy and X-ray reflectometry. UV/Vis absorption and reflection measurements complete our work. The metal layer formation can be described by applying an appropriate growth model based on our earlier work. [4] The model is refined in an iterative process of GISAXS simulations and data fitting. Comparing the deposition behavior of typical electrode materials on thin films of photoactive organic materials helps to understand their influence on the respective device performance.

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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, *Iradwikanari Waluyo*, Brookhaven National Laboratory **INVITED**

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 Cu₂O/Cu(111) by CO, in which the reduction of Cu⁺ to Cu 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 Cu₂O/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 Artyushkova*, 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 (PEMFC). 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 nitrogens, such as pyridinic, coordinated to iron and hydrogenated nitrogens (pyrrolic 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 are of ultimate importance for elucidating the oxygen reduction reaction mechanism.

1. Artyushkova, K., et al., *Oxygen Binding to Active Sites of Fe-N-C ORR Electrocatalysts Observed by Ambient-Pressure XPS*. The Journal of Physical Chemistry C, 2017. **121**(5): p. 2836-2843.

9:00am AS+BI+SA+SS-ThM-4 In situ Monitoring of Electrochemically Generated Carbene by XPS, *Pinar Aydogan Gokturk*¹, *S Donmez, Y Turkmen, B Ulgut, 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 voltammogram 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 vapor 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 Artyushkova*, University of New Mexico; *C Ngo, 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 graphitic content were synthesized by a solvothermal treatment of resorcinol, 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 compositions and properties were produced. Differences in composition and structure 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

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¹ A. Serov, K. Artyushkova, E. Niangar, C. Wang, N. Dale, F. Jaouen, M.-T. Sougrati, Q. Jia, S. Mukerjee, and P. Atanassov, *Nano Energy* **16**, 293 (2015).

² K. Artyushkova, I. Matanovic, B. Halevi, and P. Atanassov, *J. Phys. Chem. C* **121**, 2836 (2017).

³ Q. Jia, N. Ramaswamy, H. Hafiz, U. Tylus, K. Strickland, G. Wu, B. Barbiellini, A. Bansil, E.F. Holby, P. Zelenay, and S. Mukerjee, *ACS Nano* **9**, 12496 (2015).

⁴ N.P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai, and M. Jaroniec, *Chem. Mater.* **26**, 2820 (2014).

11:00am **AS+BI+SA+SS-ThM-10 Real-time Photoelectron Spectroscopy Observation of Oxidation and Reduction Kinetics of Ni(111) Surface**, *Ryo Taga, S Ogawa, Y Takakuwa*, Tohoku University, Japan

Nitrogen contained in the air is oxidized and then harmful nitrogen oxide (NO_x) is formed in the combustion chamber of engine. Accordingly, the exhaust gas which contains NO_x is purified by catalysts. However, platinum group metals, whose prices are likely to rise by the depletion of resources in the future, are used as the catalysts, so the reduction of the amount used is an important matter for industrial and environmental fields. On the other hand, it has been already known that Ni has an effect to NO_x reduction, but its catalytic ability disappears when the Ni surface is oxidized. If O atoms on the Ni surface can be efficiently desorbed, Ni is expected as a catalyst for NO reduction. In the previous studies, some of researches have studied about reduction of oxidized Ni surfaces, but the relation between oxide reduction kinetics and behavior of O atoms has not yet been clarified. In this study, the oxidation and reduction kinetics on Ni(111) surfaces was investigated by real-time ultraviolet photoelectron spectroscopy (UPS). to investigate the amount of O atom adsorption and the changes of work function.

The experiments were performed using UPS apparatus with base pressure of $\sim 3 \times 10^{-8}$ Pa. The Ni(111) surface was firstly cleaned by the Ar⁺ ion bombardment, and the annealed at 600°C. O₂ gas (1×10^{-5} Pa) was directly introduced to UPS apparatus at the sample temperature of 100°C. After the end of the introduction of O₂ gas, the sample heated up to and H₂ gas (1×10^{-5} Pa) was introduced in order to investigate the Ni oxide reduction process. The photoelectron spectra were measured repeatedly each 72 s during oxidation and reduction.

From the time evolution of O 2p photoelectron spectra, we obtained the O 2p uptake curve and the change in work function. When O₂ gas was introduced, O 2p intensity increases linearly, so it turned out that the oxidation of Ni(111) surfaces was a zero order reaction. After introduction of H₂ gas, O 2p intensity decreases gently for about 500 s and then decreased rapidly. On the other hand, the work function slightly increased and then rapidly decreased. The work function reaches the same value on the clean Ni(111) surface. Therefore, Ni oxide can be reduced completely using H₂ gas.

These changes after introduction of H₂ gas can be divided into two areas. In the first area, O atoms are drawing from subsurface because of slight increase of work function. In the second area, then, it is suggested that the reduction progresses and the clean Ni surface area enlarges as like to island growth. In the symposium, we will discuss the reduction process of the oxidized Ni surface by NO gas.

11:20am **AS+BI+SA+SS-ThM-11 Comparison of Initial Oxidation Kinetics between p- and n-type Si(001) Surfaces Studied by Real-time Photoelectron Spectroscopy**, *Yuki Sekihata, S Ogawa*, Tohoku University, Japan; *A Yoshigoe*, JAEA, Japan; *R Taga*, Tohoku University, Japan; *S Ishidzuka*, National Institute of Technology, Akita College, Japan; *Y Takakuwa*, Tohoku University, Japan

An oxidation reaction is the "trade" of electrons between oxygen and other materials, therefore it is thought that there is a difference in the oxidation kinetics on between p-type and n-type Si substrates. In the previous researches about the kinetics of the thermal oxidation of Si, the oxidation rate have not taken account of the difference of conduction type because the thermal oxidation was performed in high temperature region above 600°C named intrinsic region where the intrinsic carrier concentration becomes comparable to the donor or acceptor concentration. On the other hand, oxidation temperature becomes lower to form thin oxide films below 1nm. Therefore, we believe that the difference of conductivity affects an oxidation kinetics on the Si(001) surfaces, but there is no oxidation reaction models that takes into account the difference of conductivity. In this study, we investigated the oxidation reaction kinetics on p- and n-type Si surfaces using real-time ultraviolet photoelectron spectroscopy.

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^{18} atoms/cm³ so extrinsic region can be kept in the high temperature region even below 700°C. These samples were oxidized using O₂ gas at the pressure of 1.0×10^{-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 changes 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 show also the difference of oxide states between them.

11:40am **AS+BI+SA+SS-ThM-12 Co-Pyrphyrin on Cu₂O(111) and TiO₂(110): Properties and Stability under Near Operando Conditions**, *Zbynek Novotny, W Zabka, M Hotz, D Leuenberger*, University of Zurich, Switzerland; *L Artiglia, F Orlando, M Ammann*, Paul Scherrer Institut (PSI), Switzerland; *J Osterwalder*, University of Zürich, Switzerland

The pyridine-based macrocycle Co-pyrphyrin (Co-Pyr) is a promising molecular water reduction catalyst recently synthesized at the University of Zurich [1]. We investigated Cu₂O(111) and TiO₂(110) substrates covered with a complete monolayer of Co-Pyr at pressures spanning from ultra-high vacuum (UHV) up to near ambient pressures of 1 mbar of water vapor. To study the surface photovoltage (SPV) effect, samples were illuminated with UV laser light through the electron spectrometer lens system. Both under UHV and water pressures up to 1 mbar, SPV-induced shifts of the order of $\Delta E_k = +120$ meV were observed in case of Cu₂O(111), while for TiO₂(110), much smaller SPV shifts of -0.12 meV were observed. X-ray absorption spectroscopy (XAS) of the Co L3-edge in dependence of illumination and water exposure was used to monitor the electronic structure of the Co metal center of Co-Pyr molecules. Comparison to simulated XAS spectra reveals that on the TiO₂(110), the Co centers partially transform from a +2 to +1 oxidation state upon exposure to water, while on the Cu₂O(111), the Co remains in the +2 oxidation state irrespective of the water exposure. Our measurements provide insights into the stability and behavior of the Co-Pyr molecules studied under near operando conditions, further stimulating the use of these molecular catalysts in the next-generation of solar fuel cells.

[1] Joliat, E et al., *Dalton Transactions* **2016**,45 (4), 1737-1745.

Biomaterial Interfaces Division

Room 12 - Session BI+AS+SA-ThM

Characterisation of Biological and Biomaterial Surfaces

Moderators: Daniel Graham, University of Washington, Tobias Weidner, Aarhus University, Denmark

8:00am **BI+AS+SA-ThM-1 Lipid Involvement in the Regenerative Processes of *Dugesia dorotocephala* - A GCIB ToF-SIMS Imaging Study**, *Tina Angerer, 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 re-growing a new flatworm. 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.^[1] 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.

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Using the J105-3D Chemical Imager, (Ionoptika Ltd) equipped with a 40 keV gas cluster ion beam (GCIB), molecules with sizes up to 2000 Da can be localized at a cellular scale, with spatial resolutions better than 3 μm .^[2] Since ToF-SIMS is a label free technique, it can be used in an untargeted discovery approach which, in biological samples, is mainly used to study lipid distributions.

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.^[3] 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.

[1] T. H. Ong, *et al.*, *J Biol Chem* 2016, 291, 8109-8120.

[2] T. B. Angerer, *et al.*, *Int J Mass Spectrom* 2015, 377, 591-598.

[3] F. Meyer, *et al.*, *Biochim Biophys Acta* 1970, 210, 257-8.

8:20am **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.

8:40am **BI+AS+SA-ThM-3 Applications of XPS for Novel Biomaterial Systems**, *Jonathan Counsell, S Coultas, 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 [1]. 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.

[1] Donald R. Miller and Nikolaos A. Peppas, *Journal of Macromolecular Science, Part C Vol. 26*, Iss. 1, 1986

9:20am **BI+AS+SA-ThM-5 Surface Characterization of Polymer Scaffolds: Understanding Surface Modification and Biological Interactions**, *Michael Taylor*, University of Washington; *M Hawker, M Mann*, Colorado State University; *G Hammer*, University of Washington; *E Fisher*, Colorado State University; *D Graham, L Gamble*, University of Washington

Biopolymers show increasing usage in medical device technologies including joint replacement, stents and tissue engineered supports. (polymer scaffolds). Barriers to successful use of biopolymer usage for medical devices can include ineffective interaction of biological systems with the biopolymer and biofilm formation. Historically, developing medical devices with antibacterial properties have involved inclusion of silver or copper dopants as they facilitate bacterial membrane rupture. Bacteriostatic coatings provide an alternative approach by generating a hydrophobic surface that prevents colonisation by reversible adhesion via van der Waals forces prior to anchoring strongly with adhesion structures such as pili. Plasma enhanced chemical vapor deposition (PECVD) is a cheap yet powerful method of introducing chemical functionalities to surfaces as the low temperature high energy process may be used to couple a variety of monomers to biomaterial surfaces. Previous evidence provided by Fisher and coworkers showed that PECVD may be utilised to produce antifouling coatings by modifying polycaprolactone (PCL) with fluorinated organic compounds¹, however the porous morphology of scaffolds required for vascularisation also provides multiple points of attachment for the critical first step in biofilm formation. It is therefore necessary determine the effectiveness of PECVD throughout the scaffold. For this we employ time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) to analyse the surface modification of porous polymer scaffolds.

ToF-SIMS imaging coupled with X-ray photoelectron spectroscopy (XPS) provides a powerful combination of high resolution imaging and elemental quantitative analysis that allows a detailed analysis of the surface. Herein we apply this combination of analysis methods for the determination and quantification of fluorocarbon distribution across a PCL scaffold modified with octafluoropropane by PECVD, determining that a treatment time of 20 minutes introduces a homogeneous distribution of fluorocarbon film throughout the construct cross section whereas lower treatment times produces a gradient distribution of fluorocarbon, as measured via CF^+ and CF_3^+ signals

(1) Hawker, M. J.; Pegalajar-jurado, A.; Fisher, E. R. Conformal Encapsulation of Three-Dimensional, Bioresorbable Polymeric Scaffolds Using Plasma-Enhanced Chemical Vapor Deposition. **2014**.

9:40am **BI+AS+SA-ThM-6 Seawater Bacteria on Technical Surfaces: Lateral and Vertical Adhesion Forces and Nanomechanical Properties**, *N Davoudi, K Huttenlochner*, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany; *C Schlegel, M Huster*, University of Kaiserslautern, Institute of Bioprocess Engineering, Germany; *Christine Müller-Renno*, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany; *R Ulber*, University of Kaiserslautern, Institute of Bioprocess Engineering, Germany; *C Ziegler*, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, Germany

Biofilms are often unwanted, but can also be utilized in biofilm reactors. In such a reactor different forces act on the cells: lateral forces by flow, forces perpendicular to the interface which dominate the first contact and the biofilm formation, and forces on the cell-wall by turgor pressure which influence the viability of the cells. The interplay of these forces plays a major role in the establishment of a biofilm.

Here, we report on the seawater bacterium *Paracoccus seriniphilus* on titanium and glass. Microstructured titanium is our substrate of choice in the reactor. We hence have to understand the influence of wettability, roughness, defined structures, and environmental conditions such as pH and ionic strength on the viability as well as the bacterial attachment and detachment.

In a first set of experiments, the turgor pressure of the bacteria was determined as a function of pH and salinity by measuring force-distance curves with a scanning force microscope (SFM). As a seawater bacterium, *P. seriniphilus* can easily adapt to saline conditions and can survive at NaCl concentrations up to 100 g L^{-1} . Depending on the ionic strength the turgor pressure and thus the elasticity and size of the cell changes. *P. seriniphilus* has its optimum pH at 7, but at pH 4 the results point to an active adaption mechanism to acidic conditions. The results at pH 11 show that *P. seriniphilus* cannot adapt to alkaline conditions.

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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 attachment 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 Valtiner**¹, 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 HIs 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)_n 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 $k_B T$ per leucine. In good agreement, simulations indicate a similar trend with 2.1 $k_B T$ per leucine, while also providing a detailed molecular view into HIs.

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 unbinding 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.

[2] T. Utzig et al. in *Langmuir*, 31(9) (2015), 2722.

[3] T. Utzig, P. Stock et al. in *Angewandte Intl.* (2016).

[4] P. Stock et al. in *ACS Nano*(2017), 11 (3), 2586.

11:40am **BI+AS+SA-ThM-12 Quantitative Characterization of Bacterial Cells in Solution and on Surfaces**, C Sousa, K Jankowska, L 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 *Staphylococcus 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 apparent size of individual *S. aureus* bacteria changes dramatically as they are prepared for measurements with increased spatial resolution: from confocal optical microscopy, to environmental scanning electron microscopy (SEM), to SEM 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 at 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 metallireducens* 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 Flaherty, 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 PH₃ adsorption and annealing treatments followed by Auger electron spectroscopy to determine the P:Ru ratio. Synthesized P_{0.4}-Ru(0001) surfaces have a (r7xr7) low energy electron diffraction pattern and appear to resemble the (111) facet of bulk Ru₂P 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

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compared to Ru, suggesting that P atoms decrease the extent of electron exchange between Ru surfaces and adsorbates (i.e., CO and NH₃).

Results from temperature programmed reaction (TPR) of C₁-C₄ carboxylic acid decomposition on Ru(0001) and P_{0.4}-Ru(0001) surfaces indicate that both P atoms and the length of alkyl substituents on carboxylic acids (i.e., R = H, CH₃, CH₂CH₃, and CH₂CH₂CH₃) alter the intrinsic activation energy (E_a) of bond ruptures. On both surfaces, TPR and reactive molecular beam scattering (RMBS) 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 CO₂ (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 CO₂ 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_{0.4}-Ru(0001) (i.e., slope m = 0.2). The RMBS results from formic acid in the presence of P atoms show a higher production of CO than CO₂, which reflects the catalytic consequences of the differences between the C-H and C-O bond rupture energy barriers on P_{0.40}-Ru(0001) and those for Ru(0001). Collectively, these results suggest that P atoms alters the production selectivity of CO and CO₂ through a greater increase 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.¹ 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 bound 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 H₂O in UHV occurs on the nanoclusters, which is negligible on unreconstructed Cu(111). Previously the splitting of H₂O was thought to be a geometric effect caused by the nanoclusters as under UHV conditions CO does 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 H₂O partial pressure is increased in the IR cell to 2 × 10⁻⁸ Torr and flowed over the reconstructed Cu(111) crystal. The RAIR spectra indicates there is a reactive CO species that interacts with H₂O to create formaldehyde. This is further confirmed by observing formaldehyde with temperature programmed desorption following H₂O 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-carbonyls, which can be present in the CO bottle, or produced in the reaction cell. The possibility of Fe as the cause for the CO bound in UHV will be presented.

1. Eren, B.; Zherebetsky, D.; Patera, L. L.; Wu, C. H.; Bluhm, H.; Africh, C.; Wang, L.-W.; Somorjai, G. A.; Salmeron, M. Activation of Cu(111) Surface by Decomposition into Nanoclusters Driven by CO Adsorption. *Science* **2016**, *351*, 475 LP - 478.

8:40am HC+SA+SS-ThM-3 Thermal and Plasma Heterogeneous Catalysis Compared: CO₂ and Hydrocarbon Dry Reforming, Q Huang, D Zhang, Center of Interface Dynamics for Sustainability, Chengdu, PR China, China; E Schuler, M Ronda Lloret, G Rothenberg, N Shiju, van 't Hoff Institute for Molecular Sciences, Amsterdam, The Netherlands, Netherlands; Aart Kleyn, Center of Interface Dynamics for Sustainability, PR China, China

INVITED

Endothermic catalytic reactions require operation at elevated temperatures. The heating required is usually obtained by combustion of hydrocarbons and contributes to CO₂ emission. Instead electricity obtained in a sustainable should drive the reaction. In addition, it is desirable that the energy transfer involved is done in a bond specific manner. Plasma

excitation and dissociation of molecules can serve this purpose. In plasma, all molecular degrees of freedom are not in equilibrium and dissociation of CO₂ can be realized much more efficiently than in thermodynamic equilibrium. There is a preferential vibrational excitation of CO₂.

In Chengdu we use a plasma chemical reactor with mass spectroscopy, infrared spectroscopy, optical emission spectroscopy and a Langmuir probe to study the characteristics of the plasma, reaction products and the catalyst. In Amsterdam we use a thermal reactor and gas chromatography to study reaction products. The reactions are carried out at pressures of several hundreds of Pa up to atmospheric in Ar buffergas. Catalysts are prepared in the usual way.

The simplest reaction studied in the plasma reactor is the dissociation of CO₂ into CO and O₂. 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 Al₂O₃ 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 C₂ 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 CH₄ with CO₂ in the plasma reactor we find that addition of an oxidic catalyst does not enhance the yield of CO + H₂. In the case of dry reforming of butane (C₄H₁₀) to yield butene (C₄H₈), plasma reforming with or without catalyst does shows only small conversion. Mainly cracking of butane into C₂H_x 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 complexes 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 CO₂ and H₂ [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

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Reduction Reaction, which is really the limiting reaction in Proton Exchange Membrane Fuel Cells. Here we have found entirely new classes of electro-catalysts 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].

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11:40am **HC+SA+SS-ThM-12 Chemisorption and Oxidation of H₂ on IrO₂(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 IrO₂ surfaces is central to improving applications of electrocatalysis as well as exploiting the high-reactivity of IrO₂ 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 IrO₂(110) surfaces. We find that H₂ dissociation is highly facile on s-IrO₂(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-IrO₂(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 recombinative desorption processes, respectively. We present evidence that H₂ dissociation on IrO₂(110) occurs through a mechanism wherein H₂ σ-complexes adsorbed on the coordinatively-unsaturated (cus) Ir atoms serve as precursors for H₂ dissociation. We show that oxygen atoms adsorbed on the cus-Ir sites, so-called on-top O-atoms, hinder H₂ dissociation on IrO₂(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 H₂O formation on stoichiometric and O-rich IrO₂(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 at 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_m/(LuFe₂O₄)₁ 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].

[1] J. A. Mundy *et al.*, *Nature* **537**, 523 (2016).

[2] Y. Cao *et al.*, *npj Quantum Materials* **1**, 16009 (2016).

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 Manfredda, M Kiskinova*, Elettra-Sincrotrone Trieste, Italy; *M Klauui, 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 100s 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 Würle*, Technische Universität München, Germany; *W Ohm*, DESY, Germany; *H Iglev*, 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 should 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)thiophene-2,5-diy] (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

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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.

[1] Körstgens et al., *Nanoscale* 7, 2900 (2015)

9:40am **SA+AC+MI-ThM-6 New Instrumentation for Spin-integrated and Spin-resolved Momentum Microscopy – METIS and KREIOS**, *Thomas Schulmeyer*, *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_k) 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_k) 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_k 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 **INVITED**

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 **INVITED**

Recent advances in dynamics studies of condensed matter by X-ray photon correlation methods will be discussed. Classical X-ray Photon Correlation Spectroscopy (XPCS) requires 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.

Bold page numbers indicate presenter

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 Valtiner, M: BI+AS+SA-ThM-10, **32**
 van der Laan, G: AC+AS+SA+SU-MoA-1, 3
 Van Humbeck, J: AC+AS+SA-TuM-10, 8
 Vasco, J: AS+2D+NS+SA-WeA-12, 24
 Vaz, C: MI+SA-WeM-10, **20**
 Veillerot, M: SA+AS+HC+SS-TuA-10, 15
 Vianco, P: AS+BI+MI+NS+SA+SS-WeM-12, 19
 Vidal, V: SA+AS+HC+SS-TuA-12, 16
 Viro, F: AC+MI+SA+SU-TuA-3, 12
 Vlasak, P: AS+BI+MI+NS+SA+SS-WeM-5, **18**
 Vogel, J: SA+AS+HC+SS-WeA-9, **28**
 von Gundlach, A: BI+AS+MI+SA-TuA-11, 14
 Vorng, J: BI+AS+MI+SA-TuA-10, 13
 Vurpillot, F: AS+2D+NS+SA-WeA-3, 23
 — W —
 Wadayama, T: HC+SA+SS-WeA-1, **25**
 Walkup, D: MI+2D+AC+SA+SS-TuM-2, 8
 Waluyo, I: AS+BI+SA+SS-ThM-1, **29**
 Wang, C: AS+2D+NS+SA-WeA-7, 23; SA+MI-
 TuM-6, 10
 Wang, J: AS+BI+MI+NS+SA+SS-WeM-13, **19**
 Wang, S: AC+AS+SA-TuM-10, 8
 Wang, Y: 2D+AS+SA+SP-TuM-11, 7
 Waser, R: SA+AS+HC+SS-WeA-7, 27
 Watanbe, K: MI+2D+AC+SA+SS-TuM-2, 8
 Wdowik, U: AC+MI+SA+SU-TuA-9, 12
 Weaver, J: HC+SA+SS-ThM-12, 34
 Weiland, C: SA+AS+HC+SS-TuA-9, **15**
 Weiss, A: AC+AS+SA-TuM-3, 7
 Weiss, P: MI+SA-WeM-5, 20
 Weng, T: AC+AS+SA+SU-MoA-1, 3
 Werner, C: BI+AS+MI+SA-TuA-1, **12**
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 Wiell, T: SA-TuP-3, 17
 Wietstruk, M: SA+AC+MI-ThM-6, 35
 Wilhelm, F: MI+2D+AC+SA+SS-TuM-6, 9
 Woicik, J: SA+AS+HC+SS-TuA-9, 15
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 — Y —
 Yaita, T: AC+AS+SA-TuM-10, 8
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 Yang, H: MI+2D+AC+SA+SS-TuM-3, **8**
 Yang, P: AC+MI+SA+SU-MoM-5, **1**
 Yang, Y: BI+AS+MI+SA-TuA-11, 14
 Ye, M: MI+SA-WeM-5, 20
 Yi, J: MI+BI+EM+SA-MoA-4, 4
 Yngman, S: SA+AS+HC+SS-TuA-3, 14
 Yoshigoe, A: AS+BI+SA+SS-ThM-11, 30;
 SA+AS+HC+SS-WeA-11, 28
 Yousefi Sarraf, S: MI+2D+AC+SA+SS-TuM-12,
 9
 Yu, S: AC+AS+SA+SU-MoA-1, 3
 Yu, X: AS+BI+MI+NS+SA+SS-WeM-1, 18;
 AS+BI+MI+NS+SA+SS-WeM-13, 19;
 BI+AS+SA-ThM-13, **32**
 Yulaev, A: SA+AS+HC+SS-WeA-3, 27
 — Z —
 Žaba, T: AS+2D+NS+SA-WeA-10, 24
 Zabel, H: SA+AC+MI-ThM-3, 34
 Zabka, W: AS+BI+SA+SS-ThM-12, 30
 Zacharias, H: MI+SA-WeM-12, 21; MI+SA-
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 Zeigermann, P: SA-TuP-3, 17
 Zhai, Z: AS+2D+NS+SA-WeA-7, 23
 Zhang, C: BI+AS+MI+SA-TuA-4, 13
 Zhang, D: HC+SA+SS-ThM-3, 33
 Zhang, F: 2D+AS+SA+SP-TuM-10, **6**;
 AS+BI+MI+NS+SA+SS-WeM-1, 18
 Zhang, H: 2D+AS+SA+SP-TuM-5, **6**;
 SA+AS+HC+SS-WeA-1, 27
 Zhang, Y: AS+BI+MI+NS+SA+SS-WeM-13, 19;
 SA+MI-TuM-13, 11
 Zheng, H: 2D+AS+SA+SP-TuM-10, 6
 Zhitenev, N: MI+2D+AC+SA+SS-TuM-2, 8
 Zhu, C: SA+MI-TuM-6, 10
 Zhu, Z: AS+BI+MI+NS+SA+SS-WeM-1, 18;
 AS+BI+MI+NS+SA+SS-WeM-13, 19
 Ziegler, C: BI+AS+MI+SA-TuA-3, **13**;
 BI+AS+SA-ThM-6, 31
 Zou, Q: MI+BI+EM+SA-MoA-4, 4