Tuesday Afternoon, November 11, 2014

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room: 312 - Session SA-TuA

Free Electron Laser and Synchrotron Studies at the Molecule-Surface Interfaces
Moderator: Zahid Hussain, ALS-LBNL

2:20pm **SA-TuA1 FEL-Based Techniques to Explore Photochemistry and Transient States of Molecules on Surfaces**, ***Wilfried Wurth***, Universität Hamburg, Germany **INVITED**

New light sources based on linear accelerators such as the free-electron laser FLASH at DESY in Hamburg in the extreme ultraviolet, the Linac Coherent Light Source LCLS in Stanford as the world´s first x-ray laser or FERMI at ELETTRA in Trieste as the first fully externally seeded free-electron laser provide ultrashort, extremely powerful short wavelength pulses with unprecedented coherence properties.

With these new sources it is possible to extend the well-established x-ray spectroscopic techniques for the investigation of the static electronic structure of matter like e.g. photoelectron and x-ray emission spectroscopy to probing the evolution of the electronic structure after controlled excitation in the time domain. The talk will review recent time-resolved x-ray spectroscopy experiments illustrating the opportunities for the study of ultrafast dynamics at surfaces. I will mainly discuss results which have been obtained in the framework of a large international Surface Science Collaboration at LCLS including groups from the US (SLAC in Stanford), from Sweden (University Stockholm), from Denmark (Danish Technical University), and from Germany (Fritz-Haber Institute and Helmholtz Center Berlin, and the Center for Free-Electron Laser Science (CFEL) at the University of Hamburg). These results show that with the new sources it is possible to characterize transient intermediates in surface reactions. Furthermore first steps towards monitoring surface reactions in real-time will be illustrated.

This work has been supported by German Ministry for Education and Science through the priority program FSP-301: “FLASH: Matter in the Light of Ultrashort, Extremely Intense X-ray Pulses”

References:

M. Dell’Angela et al., Real-Time Observation of Surface Bond Breaking with an X-ray Laser, Science 339, 1302 (2013)

M. Beye et al., Selective Ultrafast Probing of Transient Hot Chemisorbed and Precursor States of CO on Ru(0001), Phys. Rev. Lett. 110, 186101 (2013)

T. Katayama et al., Ultrafast soft X-ray emission spectroscopy of surface adsorbates using an X-ray free electron laser, Journal of Electron Spectroscopy and Related Phenomena 187, 9 (2013)

3:00pm **SA-TuA3 Real-time X-ray Photoelectron Spectroscopy Studies of Electronic Dynamics at Molecule-Semiconductor Interfaces**, ***Oliver Gessner***, Lawrence Berkeley National Laboratory **INVITED**

Interfacial charge transfer processes in molecular and nanoscale systems play an increasingly important role in emerging concepts for renewable energy technologies. Rational design decisions, however, rely on our capability to monitor the pathways of charge carriers on an atomic scale and with a temporal resolution that is commensurate with the timescales of interfacial electron motion. We introduce a new approach to characterize the location of a migrating electron at a molecule-semiconductor interface with sub-nanometer spatial sensitivity and sub-picosecond temporal resolution. Employing the unique capabilities of the Linac Coherent Light Source (LCLS) X-ray Free Electron Laser we use femtosecond time-resolved X-ray photoelectron spectroscopy (tr-XPS) to monitor the nature of an intermediate state that precedes free charge carrier generation in dye-sensitized ZnO nanocrystals after photoexcitation with visible light. Using the element specificity of inner-shell photoemission lines and, in particular, their sensitivity to transient local valence electronic structures, tr-XPS employs the Ru center of the dye molecule as a local reporter atom to provide a unique perspective on ultrafast interfacial charge flow. The underlying physics are explored in a concerted effort with constrained density functional theory (CDFT) calculations of the interfacial electronic structure. The results are discussed with respect to a significantly reduced rate of free charge carrier generation in N3/ZnO systems compared to other material combinations such as N3/TiO_2.

Femtosecond time-resolved experiments at the LCLS are complemented by a new picosecond time-resolved XPS effort at the Advanced Light Source (ALS). Using a novel time-stamping technique in combination with a high-power picosecond laser system, tr-XPS experiments on dye-sensitized semiconductor substrates can be performed with up to MHz repetition rates in all operating modes of the ALS (multi-bunch and two-bunch). The measurements simultaneously monitor chemical shifts of particular photolines and transient surface photovoltages of the semiconductor substrate. Results will be discussed with respect to a possible correlation between intramolecular electron dynamics and transient interfacial charge carrier concentrations in the semiconductor. Routes and first steps toward the implementation of *in operando* X-ray studies of interfacial photoelectrochemical processes will be outlined.

4:20pm **SA-TuA7 Unraveling Topological Properties of Spintronic Materials Using Coherent X-rays**, ***Sujoy Roy***, Lawrence Berkeley National Laboratory **INVITED**

Understanding new topological states in condensed matter systems is a current research topic of tremendous interest due to both the unique physics and their potential in device applications. The topological magnetic phases have exotic spin texture, and in some cases can be moved coherently over macroscopic distances with very low currents. Recently discovered skyrmions is an example of such a topological phase that manifest in magnetic systems as a hexagonal lattice of spin vortices. In this talk we will discuss our observation of the skyrmions using resonant soft x-ray scattering in Cu_2SeO_3 and demonstrate the unexpected existence of two distinct skyrmion sub-lattices that arise from inequivalent Cu sites with chemically identical coordination numbers and valency. The skyrmion sublattices are rotated with respect to each other implying a long wavelength modulation of the lattice. The coupled response of these sub-lattices to external magnetic field suggests a secondary interaction term that has not been predicted. We will also describe an artificial spin ice system whose origin lies in geometrical frustration that comes from the topology of a well-ordered structure rather than from disorder. We observed that under certain applied magnetic field the spin ice exhibits a magnetic structure that can impart orbital angular momentum into the photon beam thereby creating a vortex beam. Further, the vortex beam can be manipulated by an applied magnetic field. Creating an x-ray vortex beams may enable new x-ray based techniques such as coherent control of excitations in quantum material, trapping and rotation of quasiparticles or biomolecules with free electron laser x-ray sources.

Work is funded by U.S. DOE.

5:00pm **SA-TuA9 Where are the Electrons? Charge Transfer and Dissociation from a Femtosecond Electronic-Structure Perspective**, ***Philippe Wernet***, Helmholtz-Zentrum Berlin (HZB), Germany **INVITED**

Molecular structure and chemical bonding determine the dynamic pathways of molecules in their multidimensional landscapes and hence define the outcome of chemical reactions. Characterizing chemical bonding in short-lived reaction intermediates and transient states of molecules is hence the key to understanding chemical selectivity.

Spectroscopy with femtosecond light pulses with energies ranging from the ultraviolet to the x-ray regime enables a unique approach to the atomic-scale chemical dynamics as it allow for a complete mapping of the electronic structure of atoms and molecules during chemical reactions [1]. Time-resolved femtosecond x-ray spectroscopy in particular reveals chemical bonding both in real time of the reaction and from the atom’s perspective in an element-selective way [2].

Here we present our view on charge-transfer and dissociation reactions both in the gas phase and in solution from a femtosecond electronic-structure perspective. We apply femtosecond laser pulses from laboratory laser sources and from large scale x-ray free-electron lasers to map the electronic structure evolution in prototypical systems. Our results reveal how the transient electronic structure and the nuclear dynamics are coupled and they elucidate the role of the solvent from a chemical-bonding perspective.

Detailed insight into the various cases is discussed and an outlook for the investigation of chemical reaction dynamics with x-ray laser spectroscopy is given.

References

[1] Ph. Wernet, M. Odelius, K. Godehusen, J. Gaudin, O. Schwarzkopf, W. Eberhardt, "Real-time evolution of the valence electronic structure in a dissociating molecule", Phys. Rev. Lett. 103, 013001 (2009).

[2] Ph. Wernet, "Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions", Phys. Chem. Chem. Phys. 13, 16941 (2011).

5:40pm **SA-TuA11 Layer Speciation and Electronic Structure Investigation of Hexagonal Boron Nitride Thin Film by Scanning Transmission X-ray Microscopy**, ***Jian Wang***, Canadian Light Source Inc., Canada, *Z. Wang*, University of Western Ontario, Canada, *H. Cho*, *M.J. Kim*, Korea Institute of Science and Technology, Republic of Korea, *T.-K. Sham*, University of Western Ontario, Canada, *X. Sun*, Soochow University, China

Thin films of hexagonal boron nitride (hBN) exhibit a honey cone structure similar to that of graphene, with sp^2 hybridized boron and nitrogen atoms alternately bonded in the basal plane. This unique structure leads to some excellent properties such as high chemical and thermal stabilities, enhanced thermal and electrical conductivity in the basal plane, and versatile doping capabilities. Thus hBN thin films have attracted increasing attentions in many fields. However, unlike graphene, the partly ionic B-N bond in hBN reduces electron-delocalization and creates a large band gap (5.2 eV) in the ultraviolet (UV), making hBN a wide band gap semiconductor and a promising deep UV light emitter. Therefore, an in depth understanding of the morphology and the electronic structure of individual hBN thin films will be of great importance in the development of sophisticated technologies. Synchrotron based scanning transmission X-ray microscopy (STXM) using a nanoscaled focused soft X-ray beam (~30 nm) provides an excellent combination of microscopic examination and chemical/electronic structure speciation via XANES spectroscopy for individual nanomaterials. In this work, chemical imaging, thickness mapping and layer speciation have been performed on a multilayered CVD hBN film with thickness from single layer up to 9 layers by STXM. Spatially-resolved XANES directly from discrete layers have been extracted and compared. Notably a double feature σ* exciton state and a stable high energy σ* state were observed at the boron site, and the boron projected σ* DOS, especially the first σ* exciton, is sensitive to surface modification, particularly in the single layer regions which show detectable contaminants and defects. Nitrogen site has shown no exciton character. The distinct exciton effect on boron and nitrogen was interpreted to the partly ionic state of hBN. Bulk XANES spectroscopy of hBN thin films was also measured to confirm the spectro-microscopic STXM result. Finally, we compare the XANES (i.e. unoccupied electronic structure) of hBN with that of graphene to elucidate the similarities and origins of the corresponding spectroscopic features.

6:00pm **SA-TuA12 Reference-free, In-depth Characterization of Nanoscaled Materials by Combined X-ray Reflectivity and Grazing incidence X-ray Fluorescence Analysis**, ***Philipp Hönicke***, *M. Müller*, Physikalisch-Technische Bundesanstalt, Germany, *B. Detlefs*, CEA-LETI, France, *C. Fleischmann*, IMEC, Belgium, *B. Beckhoff*, Physikalisch-Technische Bundesanstalt, Germany

The accurate in-depth characterization of nanoscaled layer systems is an essential topic for today's developments in many fields of materials research. Thin high-κ layers [1], gate stacks and ultra-shallow dopant profiles are technologically relevant for current and future electronic devices. Nanolaminate composites, consisting of alternating layers of different materials with a nanometer scale thickness, are being developed for energy storage and memory applications [2]. However, the metrological challenges to sufficiently characterize such complex systems require a further development of the current analytical techniques.

Synchrotron-based Grazing Incidence X-ray Fluorescence (GIXRF) analysis has already been shown to be capable of contributing to the in-depth analysis of nanoscaled materials [3,4]. Essential for the quality of the results obtained with GIXRF is the calculation of the underlying X-ray standing wave field. This requires accurate knowledge of the optical properties of the system under investigation. Usually, this cannot be obtained from tabulated data due to the complexity of the sample in terms of layer thicknesses and material combinations and because of the fundamentally different material properties at the nanoscale.

The combination of GIXRF with X-Ray Reflectometry (XRR), provides access to the optical properties of the sample and has been shown to improve the characterization reliability of GIXRF [3]. Employing the novel in-house built instrumentation [5] and radiometrically calibrated detectors at the laboratory of the Physikalisch-Technische Bundesanstalt at the BESSY II synchrotron radiation facility, this combined method allows for reference-free quantitative in-depth analysis [3,4,6]. The capabilities of the combined XRR-GIXRF method are demonstrated by means of several nanoscaled layer systems as well as ultra-shallow dopant profiles.

[1] R.D. Clark, Materials 7(4), (2014), 2913.

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[3] P. Hönicke et al., J. Anal. At. Spectrom. 27, (2012), 1432.

[4] M. Müller et al., Materials 7(4), (2014), 3147.

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[6] P. Hönicke, M. Müller, B. Beckhoff, Solid State Phenomena 195, (2013), 274.

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