2D Materials Focus Topic
Room 103B - Session 2D+MI+SA-MoM

2D Materials Characterization including Microscopy and Spectroscopy

Moderator: Matthias Batzill, University of South Florida

8:20am **2D+MI+SA-MoM1 Scanning Tunneling Microscopy and Spectroscopy of Air Exposure Effects on Molecular Beam Epitaxy Grown WSe_2 Monolayers and Bilayers***, J.H. Park,* Univeristy of California, San Diego*; S. Vishwanath,* Cornell University*; X. Liu,* University of Notre Dame*; H. Zhou,* Cornell University*; S.M. Eichfeld,* Pennsylvania State University*; S.K. Fullerton-Shirey,* University of Pittsburgh*; J.A. Robinson,* Pennsylvania State University*; R. Feenstra,* Carnegie Mellon University*; J. Furdyna,* University of Notre Dame*; D. Jena, H.G. Xing,* Cornell University*;* ***Andrew Kummel,*** University of California, San Diego

The effect of air exposure on 2H-WSe_2/HOPG was determined *via* scanning tunneling microscopy. WSe_2 was grown by molecular beam epitaxy on highly oriented pyrolytic graphite (HOPG), and afterwards, a Se adlayer was deposited *in-situ* on WSe_2/HOPG to prevent unintentional oxidation during transferring from the growth chamber to the STM chamber. After annealing at 773 K to remove the Se adlayer, STM images show that WSe_2 layers nucleate at both step edges and terraces of the HOPG. The grain boundaries and the step edges of WSe_2 ML have a bias dependence in STM imaging, consistent with difference electronic states with the defect-free terraces. After exposure air for 1 day, although the edge of WSe_2 is partially oxidized, the grain boundaries still maintain a defective electronic structure. Exposure to air for 1 week and 9 weeks caused air-induced adsorbates to be deposited on the WSe_2 surface; however, as shown for localized electronic structure measurement using scanning tunneling spectroscopy (STS), the bandgap of the terraces remained unaffected and nearly identical to those on de-capped WSe_2. The air-induced adsorbates can be removed by annealing at 523 K. In contrast to WSe_2 terraces, air exposure caused the edges of the WSe_2 to oxidize and form protrusions, resulting in a larger STS bandgap compared to the terraces of air exposed WSe_2 monolayers. The preferential oxidation at the WSe_2 edges compared to the terraces is likely the result of dangling bonds at step edges. In the absence of air exposure, the dangling edge bonds have a smaller band gap compared to the terraces and a shift of about 0.73 eV in the Fermi level towards the valence band. However, after air exposure, the band gap of the oxidized WSe_2 edges became larger about 1.08 eV that of the WSe_2 terraces, resulting in the electronic passivation of the WSe_2.

8:40am **2D+MI+SA-MoM2 Tuning the Trion Photoluminescence Polarization in Monolayer WS_2**, ***Aubrey Hanbicki,*** *K.M. McCreary, M. Currie,* Naval Research Laboratory*; G. Kioseoglou,* University of Crete*; C.S. Hellberg, A.L. Friedman, B.T. Jonker,* Naval Research Laboratory

Monolayer transition metal dichalcogenides (TMDs) such as MoS_2 or WS_2 are semiconductors with degenerate, yet inequivalent *k*-points labeled *K* and *K'* that define the direct bandgap. The valence band maximum in each valley has only one spin state in which the spins are opposite for *K* and *K'*. Consequently, one can selectively populate each valley independently with circularly polarized light and determine the valley populations via the polarization of emitted light. Monitoring changes in emitted polarization, therefore provide insights into the fundamental processes of intervalley scattering. We prepare single-layer WS_2 films such that the photoluminescence is from either the neutral exciton or the negatively charged trion [1,2]. In most TMDs, the optical polarization is small at room temperature, and we find that the neutral exciton emission indeed has zero polarization at room temperature. However, we observe a room temperature optical polarization in excess of 40% for the trion. The trion polarization always exceeds that of the exciton and exhibits a pronounced, non-monotonic temperature dependence – the polarization nearly doubles as the temperature increases from 125 K to 175 K. The observed increase in optical polarization directly correlates with a decrease in emission intensity between 125-175 K indicating that this effect is a consequence of the onset of nonradiative processes. Because this dependence involves trion systems, one can use gate voltages to modulate the polarization or intensity emitted from TMD structures. Using an applied gate voltage, we can modulate the electron density and subsequently the polarization of WS_2 trions continuously from 20-40%. Both the polarization and the emission energy monotonically track the gate voltage with the emission energy increasing by 45 meV. We discuss the role electron capture of the trion has on suppressing the intervalley scattering process. This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

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9:00am **2D+MI+SA-MoM3 Quantum Hall Effect in Graphene Visualized through Scanning Tunneling Microscopy and Spectroscopy***,* ***Adina Luican-Mayer,*** University of Ottawa, Canada **INVITED**

The ability to controllably layer atomically thin crystals into custom-made materials holds promise for realizing physical systems with distinct properties, previously inaccessible. The experimental results described in this talk seek to uncover the unique nature of the charge carriers in such few-atoms-thick materials as well as effects that interlayer coupling and disorder have on their properties. To that end we use scanning tunneling microscopy (STM) and spectroscopy (STS) experiments performed on graphene systems at low temperatures and in magnetic field. We study Landau quantization in graphene and by performing spatially resolved STM/STS we demonstrate the true discrete quantum mechanical electronic spectrum within the Landau level band near charged impurities in graphene in the quantum Hall regime.

9:40am **2D+MI+SA-MoM5 Enhancing the Electrical Conductivity of VUV-reduced Graphene Oxide by Multilayered Stacking***,* ***Yudi Tu,*** *T. Utsunomiya, T. Ichii, H. Sugimura,* Kyoto University, Japan

Reducing graphene oxide (GO), a highly oxidized graphene derivatives, by utilizing light irradiation has drawn great attention, due to its flexibility to locally fabricating conductive patterns and tuning the electrical property. We have demonstrated the reduction of GO under the 172 nm vacuum-ultraviolet (VUV) irradiation under high vacuum and combined it with mask photolithography to make reduced graphene oxide (rGO) conductive pattern at sub-μm scale.[1,2] The recovery of electrical conductivity at the reduced regions was confirmed by conductive-probe atomic force microscope (CAFM). However, further researches by applying micro Raman spectroscopy (μRS), scanning tunneling microscopy (STM) and CAFM have revealed that the pristine defects induced by the harsh oxidative synthesis of GO is unable to be repaired. On purpose to enhance the electrical conductivity of rGO pattern, generating more conductive paths for the carriers' transportation is of great importance. In this presentation, we will demonstrate the enhanced electrical conductivity in multilayered rGO sheets. The nanoscale conductive sp^2 domains in rGO are connected to construct 3-dimensional conductive paths between the multilayered sheets.

The GO-coated Si substrate was irradiated by the VUV light in the high vacuum (< 10^{-3} Pa) chamber. The CAFM current mapping revealed that GO and the derived rGO were heterogeneous hybrids of both conductive and insulating domains. Interestingly, besides the nanoscale domains distribution revealed by the previous μRS and STM results, the microscale domains distribution was also observed within the sheets, which was attributed to the uncertainly harsh oxidation synthesis. The CAFM current mapping showed obvious enhancement on the electrical conductivity of bi-layered rGO comparing with the single-layered rGO. A triangle approximate model was applied to estimate the lateral electrical conductivity of rGO sheets. It was found that the tip contact area showed no clear influence on the lateral electrical conductivity. By further measuring the current signals from both bi-layered and single-layered rGO sheets, it was found that the enhancement was not due to the parallel-connection of two rGO sheets but originated from the newly constructed 3-dimensional conductive paths between them.

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10:00am **2D+MI+SA-MoM6 Silicene-like Reconstruction via Surface Relaxation of Hexagonal-$MoSi_2$ Crystallites***,* ***Cameron Volders,*** *P. Reinke, G. Ramalingam, E. Monzami,* University of Virginia

The exciting properties of 2D materials have intrigued scientists and engineers for over a decade. A new wave of 2D materials are being explored in the scientific community, specifically, Silicene has garnered much attention for its potential in device integration. The current Silicene literature has accepted a synthetic method of depositing monolayer (ML) amounts of Si atoms onto a heated Ag (111) substrate to produce the 2D layer. Alternative substrates such as Ir (111) have been explored to obtain silicene, however, the validity of these results are still being debated.

The current work will address an approach, which is a potential alternative route for growing a silicene layer, based on the observation of a Silicene-like reconstruction (SLR) on the surface of nanometer-scale hexagonal $MoSi_2$ crystallites terminated by the (0001) plane. The bulk (0001) $MoSi_2$ surface is comprised of Si hexagons with a Mo atom in the center. The honeycomb pattern exhibited by the SLR is formed via relaxation of the (0001) plane where the Si atoms decouple from the underlying h-$MoSi_2$ crystallites. Signatures of a 'graphite-like' Si structure have been reported in literature, but have not yet been pursued in 2D materials studies. We will present an extensive study of the SLR based on Scanning Tunneling Microscopy and Spectroscopy data.

Initially, this work will describe a parameter space in which the SLR can be confidently reproduced. Mo atoms are deposited onto a Si (001) surface and annealed to grow the h-$MoSi_2$ crystallites, which is where the SLR resides. Our experimental data supports an optimal growth regime of approximately 750˚C and 3-5 ML's of Mo. The focus will then switch to demonstrating the geometrical parameters of our SLR are strikingly similar with that of the current Silicene literature. Our experimental results indicate the honeycomb pattern of the SLR corresponds to a superstructure. When comparing the lattice constant and Si-Si distance in our structure with that of silicene literature, the results strongly suggest we are observing a low-buckled silicene layer. Also included, will be a statistical treatment contributing to the validity that a surface relaxation process is the pathway by which the layer is grown. Specific features are always observed, including a well-defined 'rim' structure and defect motif, when the SLR is observed.

The final stage of this presentation will focus on addressing the electronic structure of the SLR based on STS data. A few studies have provided STS measurements indicating the observation of a Dirac-point (DP) near 0.5 eV. Our experimental results contain an intriguing feature in the same region, which will be discussed.

10:40am **2D+MI+SA-MoM8 Electron Dynamics in Two-Dimensional Materials*, Philip Hofmann,*** Aarhus University, Denmark **INVITED**

Changing the dimensionality of a material results in significant modifications of its electronic properties. This is even the case if the parent material already has a layered structure with little interaction between the layers, as in the case of graphene, bilayer graphene and single-layer transition metal chalcogenides.

While the static electronic properties of novel two-dimensional materials can be studied by standard angle-resolved photoemission spectroscopy (ARPES), investigations of the ultrafast carrier dynamics require both time- and angular resolution and thus time-resolved (TR)-ARPES. There is, moreover, the technical requirement of high photon energies since the interesting part of the aforementioned materials' electronic structure (i.e. the (gapped) Dirac cone) is placed at the two-dimensional Brillouin zone boundary. Recently, it has become possible to probe states at such high k by TR-ARPES, thanks to the arrival of ultrafast high harmonic laser sources.

Here we characterize the dynamic processes around the Dirac point in epitaxial graphene [1,2], as well as around the band gap of single layer MoS_2 [3,4] using TR-ARPES. In the graphene, we can determine and control the timescales of hot carrier scattering processes. For single layer MoS_2, we can directly measure the size of the direct band gap by pumping electrons into the conduction band minimum. We find that this band gap can be strongly renormalized, both by a static interaction with the substrate and by a dynamic screening due to a high density of excited free carriers.

References

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11:20am **2D+MI+SA-MoM10 Novel Characterization Techniques for 2D Materials: Visualizing Inherent and External Defects*, Rudresh Ghosh,*** *S.K. Banerjee, D. Akinwande,* University of Texas at Austin

Over the last decade, since the demonstration of exceptional physical, chemical and electrical properties of graphene, there has been a lot of interest in two-dimensional materials. Of these new materials significant effort has been focused on transition metal dichalcogenides (TMDs) due to their various possible applications. Initial work on TMDs, similar to that of graphene, has depended on exfoliated samples. In this work we present controlled large-area synthesis of highly crystalline few to monolayers of various TMDs (MoS2, WS2, WSe2) using both solid and gas precursors. Characterization of the TMDs are done using a combination of conventional techniques such as Raman and Photoluminescence spectroscopy, Atomic force microscopy, scanning and transmission electron microscopy. Shifts in Raman and PL spectra as a function of strain shows obvious differences between exfoliated and CVD grown material. New characterization tools with the capability of localized dielectric mapping (Microwave impedance microscopy) also show us a way to analyze defects that are inherent during CVD growth processes. Elemental identification of individual layers and their interfaces (using Time of Flight SIMS) are demonstrated as extremely useful for studying these 2d heterostructuress. Electrical device characterization and paths of optimization are also presented. Electrical characterization of the devices on various substrates is also presented.

11:40am **2D+MI+SA-MoM11 Anomalous Dynamical Behavior of Freestanding Graphene*, Paul Thibado,*** *M. Ackerman, P. Kumar, S. Singh,* University of Arkansas*; M. Neek-Amal, F. Peeters,* University of Antwerp, Belgium

Local, long-time evolution measurements of the height fluctuations of a 2D membrane allows examination of the fundamental foundations of statistical mechanics in soft condensed matter. However, such measurements have proved elusive, thereby forcing critical theoretical assumptions in our best models. We report sub-nanometer, high-bandwidth height measurements of freestanding graphene using constant-current, point-mode scanning tunneling microscopy, as a follow-up to our previous related works [1-2]. By tracking atoms directly, the ability to measure dynamic events is increased by a factor of 1000 over the present state-of-the-art membrane imaging technology. Surprisingly, the membrane velocities follow the Cauchy-Lorentz distribution consistent with a Lévy process, rather than the expected Maxwell-Boltzmann distribution. We also present molecular dynamics simulations, which illustrate spontaneous mirror buckling events that give rise to the long excursions.

Acknowledgements:

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Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 103C - Session SA+AS+MI-MoM

Advances in High-Resolution Imaging Techniques (8:20-10:20 am)/Pushing the Limits with X-Ray Spectroscopy (10:40 am-12:00 pm)

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Claus Michael Schneider, Forschungszentrum Juelich GmbH, Germany

9:00am **SA+AS+MI-MoM3 Applications of Novel Hard X-ray Nanoprobe in Nanoscience*, Gema Martinez-Criado,*** Madrid Materials Science Instititute, CSIC, Spain **INVITED**

Owing to the spatial resolution and sensitivity (i.e., signal to background ratio), nano and micro X-ray beams are emerging tools with a strong impact in nanoscience. Although the optical quality of the X-ray focusing devices has limited the progress of hard X-ray nanoprobes, recent advances in fabrication techniques have pushed the spatial resolution towards the diffraction limit. As a result, the use of nano and micro X-ray beams has begun to extend towards the atomic domain, with concomitant and continuous developments of multiple analytical tools. The study of micro/nanoscale objects, small embedded nanodomains with weak signals and/or heterogeneous structures at the nanometer scales has required the use of intense X-ray pencil beams. Additionally, stimulated by the great brilliance with reduced emittance of current third generation synchrotron sources, and new developments in X-ray detector technology, today intense nano-X-ray beams are available with a variety of focusing devices. Finally, thanks to the multiple interactions of X-rays with matter these X-ray probes can be used for manifold purposes, such as ultra-sensitive elemental/chemical detection using X-ray fluorescence/X-ray absorption, or for identification of minority phases, and/or strain fields by X-ray diffraction with nanometer resolution. In the present talk I describe how hard X-ray nanobeams are produced and exploited today for space-resolved determination of structural and electronic properties, as well as for chemical speciation of nanosized materials. Selected recent examples will range from phase separation in single nanowires to visualization of dislocations and buried interfacial defects, to domain distortions and quantum confinement effects.

10:40am **SA+AS+MI-MoM8 Extreme X-ray Flux to Probe Picosecond Dynamics*, Alfred Baron,*** RIKEN SPring-8, Japan **INVITED**

Inelastic x-ray scattering (IXS), *in principle*, provides a nearly ideal opportunity to probe dynamics on ps and sub-ps time scales via direct measurement of the dynamic structure factor, S(Q,ω). Such measurements are interesting in many areas of science, including fundamental understanding of liquid behavior, investigations of phonons in complex materials such as superconductors and ferroelectrics, and even to help determine the composition of the earth's interior. However, high-resolution non-resonant IXS measurements are *severely flux limited*.

Over the last 18 years, the author has spearheaded a program to increase the world capability for high-resolution IXS measurements through work at SPring-8 in Japan. This began with designing and constructing a beamline based on a standard insertion device [1] then progressed to a second beamline using 3x5m tandem small-gap insertion devices (IDs) [2], while in parallel, upgrading the earlier facility to a optimized small-gap ID. *This has successfully led to world-leading flux at workhorse spectrometers with ~1.25 meV resolution and 30 GHz onto the sample at 21.7 keV*, and up to 30 momentum transfers collected in parallel. Resolution as good as 0.75 meV [3] can be achieved at higher (25.7 keV) energy while medium resolution spectrometer provides in excess of 2 THz onto a sample with 27 meV resolution for measuring electronic dynamics.

The presentation will discuss aspects of the instrumentation for IXS, and recent sample science. On the instrumentation side, on top of "straightforward" issues such as sub-mK temperature control over >50 channels, installation of more that 30 tons of spectrometer, there were unique and new issues related to operating 3x5m tandem small- (6mm-) gap insertion devices [4]. On the sample side, the talk will highlight recent efforts in geoscience, where measurements at record pressures and temperatures have allowed us to constrain to composition of the Earth's core - both the outer liquid core [5] and the inner solid core. This will be complemented by a short discussion of a surprising phonon anomaly in YBa2Cu3O7-d, where phonon line-widths undergo a remarkable increase below the superconducting transition temperature [7] in what is perhaps the largest phonon anomaly observed to date in the absence of a structural phase transition.

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[7] Baron*, et al*., in preparation.

11:20am **SA+AS+MI-MoM10 Beating Complexity through Selectivity: Anti-Stokes Resonant Inelastic X-ray Scattering for Excited State Dynamics*, Alexander Föhlisch,*** University of Potsdam, Germany **INVITED**

Ultrafast electronic and structural dynamics of matter govern rate and selectivity of chemical reactions, as well as phase transitions and efficient switching in functional materials. Since X-rays determine electronic and structural properties with elemental, chemical, orbital and magnetic selectivity, short pulse X-ray sources have become central enablers of ultrafast science. Despite of these strengths, ultrafast X-rays have been poor at picking up excited state moieties from the unexcited ones. With time-resolved Anti-Stokes Resonant X-ray Raman Scattering background free excited state selectivity in addition to the elemental, chemical, orbital and magnetic selectivity of X-rays can be achieved. For low symmetry systems energetically off-set signatures dominate, and for inversion symmetric systems a clear separation between ground and excited states occurs. This unparalleled selectivity extracts low concentration excited state species along ultrafast dynamic pathways. These approaches will benefit from recent advances towards non-linear X-ray matter interaction and an outlook is given how future fourier limited X-ray laser pulses will explore ultrafast dynamics.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 103C - Session SA+AS-MoA

Frontiers of Photoemission with Synchrotron and XFEL Radiation/Advances in High-resolution Imaging Techniques

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Olivier Renault, CEA-University Grenoble Alps, France

1:40pm **SA+AS-MoA1 Photoemission with Soft and Hard X-Rays: Past, Present, and Future*, Charles Fadley,*** University of California, Davis **INVITED**

In this talk, I will begin by briefly reviewing some of the key early developments in soft x-ray photoelectron spectroscopy (XPS), angle-resolved XPS (ARXPS), x-ray photoelectron diffraction (XPD), and soft x-ray angle-resolved photoemission (ARPES). I will then consider combining these well-established methods with more recent techniques involving the tailoring of the x-ray wavefield through standing-wave (SW) excitation or total-reflection (TRXPS) to provide enhanced depth resolution and the use of hard x-ray excitation in the multi-keV regime (HXPS, HAXPES) to study bulk materials and buried layers and interfaces [1-5]. Applications to semiconductor- [1], oxide- [2.4,5], and magnetic- [2] heterostructures, as well as liquid/solid interfaces [3] will be considered. Future possibilities combining these approaches with variable polarization, as well as spin-, space-, and time- resolution will also be discussed.

Acknowledgements:

This work was supported by the U.S. Department of Energy, Contracts DE-AC02-05CH11231 at LBNL and DE-SC0014697 at UC Davis, and through the LDRD Program of LBNL.

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2:20pm **SA+AS-MoA3 Honorary Session for Prof. Charles Fadley**, *O.J. Renault,* CEA-University Grenoble Alps, France*; **Julien Rault,*** Synchrotron SOLEIL, France

This contribution is intended to honor Prof. Charles Fadely for his unvaluable work in the field of photoemission over the past 50 years and will celebrate his 75th birthday. It will immediately follow his invited talk and will take the form of 3 short talks given by some of his former students.

2:40pm **SA+AS-MoA4 Ultrafast Magnetization Relaxation Dynamics in $La_{0.66}Sr_{0.33}MnO_3$ Films*, Tommaso Pincelli,*** Università di Milano, Italy*; A.Yu. Petrov, G. Panaccione,* Laboratorio TASC, IOM-CNR, Italy*; M. Oura,* RIKEN SPring-8, Japan*; T.L. Lee,* Diamond Light Source Ltd., UK*; G. Rossi,* Università di Milano, Italy

Hole-doped rare-earth manganites, like $La_{0.66}Sr_{0.33}MnO_3$ (LSMO), display exotic phenomena such as concurrent colossal magnetoresistance and half-metallicity which originate from the interplay of charge, spin, and orbital degrees of freedom [1]. The peculiar transport properties of LSMO thin films combined with the ferromagnetic order that persists up to about 350 K [2] render such system a most technologically attractive material for spin injection: the spin polarization at the Fermi level reaches about 100% for $T<T_{Curie}$ [3].

The ultrafast manipulation of spin states in LSMO can be tested by state-of-the-art time-resolved pump-probe techniques. Previous studies by optical pump-probe spectroscopy have given evidence of photoinduced effects in ferromagnetic manganites [4].

Photo-Electron Spectroscopy (PES) allows a direct measurement of the electronic structure; time-resolved PES is able to disentangle the delicate out-of-equilibrium interplay between electronic, spin and lattice degrees of freedom [5], an essential feature in the case of highly correlated materials. HArd X-ray PhotoElectron Spectroscopy (HAXPES) extends the probing depth of PES to the bulk of the solid (tens of nm), and therefore does not suffer of the modification induced by the surface.

We present here a pump-probe HAXPES study of the relaxation dynamics of LSMO thin films. We study the structure of the Mn 2p core level and, in particular, the bulk-only screening channel proportional to the metallic and ferromagnetic state in LSMO. We observe a large and ‘slow’ reduced lineshape change up to 200 picoseconds after the IR pumping. By comparison with all-optical techniques (Time-Resolved Magneto-Optical Kerr effect, TR-MOKE) we are able to attribute the observed quenching to a collapse of magnetic order. The sudden demagnetization reduces the mobility of electrons in the solid, inducing a localization similar to a metal-insulator transition.

Since LSMO is half-metallic, the direct exchange of energy between the optically excited electrons and the magnetic order is inhibited by the absence of final states for spin-flip scattering [3]. So we can follow the relaxation dynamics as the energy is first dissipated in the lattice and then in a reduction of the magnetic order.

References

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3:00pm **SA+AS-MoA5 Inelastic Background Analysis of Haxpes Spectra for Device Technology: A Non-Destructive Tool for Accessing Deeply Buried Interfaces*, Charlotte Zborowski,*** *O.J. Renault, E. Martinez, A. Torres,* CEA, LETI, MINATEC Campus, France*; Y. Yamashita,* NIMS, Japan*; G. Grenet,* Inl, Ecl, France*; S. Tougaard,* SDU, Denmark

Recently, the advent of Hard X-ray Photoelectron Spectroscopy (HAXPES) has enabled to study deeply buried interfaces [1]. It was shown that by combining HAXPES with inelastic background analysis [2], structures at a depth >50 nm can be studied. Here, we present a study on technologically relevant High Electron Mobility power Transistors Ta/Al.

The study was performed on stacks of two metal layers of aluminum and tantalum with different thicknesses deposited on an $Al_{0.25}Ga_{0.75}N/AlN/GaN$ heterostructure [Fig. 1a]. We have used the technique to non-destructively study the activation annealing. HAXPES was performed at the Spring-8 synchrotron (Japan) using 8 keV photons.

The figure shows spectra measured around Al, Ga and Ta peaks for an as deposited sample [Fig. 1b]. The calculation of inelastic background was performed using two input parameters; the IMFP, calculated using the TPP-2M formula [3] and as the spectra present marked plasmons, after the elastic peaks, we used an average of individual inelastic cross-sections, σ, which can be determined from reflection electron energy-loss spectra. The calculation of this cross-sections’ average has been made according to a mixtures rule, involving the different crossed layers, which consists in a relevant way to analyze deeply buried layers. The figure shows how the modelling of the inelastic background is used to determine the in-depth distributions, which are found in good agreement with the TEM results. We have also successfully used this technique to study the effect of annealing on the diffusion of the elements at the interfaces.

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Part of this work was performed at the Nanocharacterization Platform of CEA-MINATEC (PFNC).

NIMS and Spring-8 is acknowledged for providing beamtime and the staff of the BL15-XU beamline for their assistance during the experiment. Cyril Guedj is acknowledged for providing TEM analysis and expertise.

3:20pm **SA+AS-MoA6 Soft X-ray ARPES Investigation of the Spin-polarized n-BaTiO$_3$/SrRuO$_3$ Buried interface***, **Julien Rault**, P. Le Fèvre, F. Bertran, J. Rebellato,* Synchrotron SOLEIL, France*; T. Maroutian, P. Lecoeur,* Université Paris-Sud - CNRS, France

The electric field control of functional properties such as spin injection is a crucial goal in oxide-based electronics. Non-volatile switching between different electron and spin transport in a tunnel junction channel can be achieved through charge accumulation or depletion at the interfaces [1, 2]. It has been recently suggested [3] that polarization-dependent spin-injection is expected at the interface between ferromagnetic SrRuO$_3$ (SRO) and semiconducting, ferroelectric n-BaTiO$_3$ (n-BTO), paving the way for adjustable spin-injection in full-oxide devices. This fascinating effect is due to the matching of the spin-dependent Fermi surface of SRO with n-doped BTO tube-like Fermi-surface [2, 3].

To investigate this phenomenon experimentally, we use angle-resolved photoemission spectroscopy (ARPES) to access the band structure of a buried n-BTO/SRO interface. A well-known limitation of ARPES comes from its very low probing depth (< 2 nm) due to the very low electron inelastic mean free path in the usual photon range of ARPES (1-100 eV). To overcome this limitation, we use soft x-ray photons and are able to access the interface Fermi surface below a 2-nm, upward polarized BTO thin film deposited on SRO.

Using 600 eV linearly-polarized photons, we measure the band dispersion of the interface SRO through the BTO band gap along with BTO bands for higher binding energies (see Fig. 1). The SRO-related bands were not visible at lower probing depth (photon energy ca. 250 eV) showing they actually come from the interface. Clear light-polarization dependence on the energy-momentum cuts along ΓX high-symmetry direction is shown in Figure 1. This is used to assign some parts of the Brillouin zone to specific orbitals with different spin-polarization. The in-plane Fermi surface of the interface SRO for k_z = Z was also acquired and showed some clear feature fitting well the calculated band structure from Liu *et al.*, see Figure 2.

These set of results is indicative of how soft x-ray ARPES is a technique of choice to probe the band structure of functional oxide interfaces. Combined with spin-resolved photoemission, which is available at our laboratory, it will help to better understand the spin polarization predicted in ferromagnetic/ferroelectric heterostructures.

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[2] Liu, X., Burton, J. D., Zhuravlev, M. Y. & Tsymbal, E. Y., *Physical Review Letters* **114**, 46601 (2015)

[3] Liu, X., Wang, Y., Burton, J. D. & Tsymbal, E. Y., *Physical Review B* **88**, 165139 (2013)

4:00pm **SA+AS-MoA8 Progress and Perspectives in Photoemission using XFEL Radiation***, **Serguei Molodtsov**,* European XFEL GmbH, Germany **INVITED**

Photoemission is today one of the most powerful techniques for investigating low-energy properties of matter from the aerosol and adsorbate nanoparticles and molecules to the surface and bulk of solid state matter with many dedicated and specialized beamlines at synchrotron radiation facilities. The upcoming ultra-brilliant FEL sources, giving access to ultrashort timescales in the fs range, in combination with the outstanding peak brilliance achieved, set the stage for novel science. Experiments on X-ray FEL sources are being pioneered and planned at low repetition rate facilities (FLASH, LCLS, SACLA, FERMI). The European XFEL that will come in early user operation already in 2017 will be characterized by laser action from 260 eV to 25 keV photon energy and above. The facility will also yield an extremely high mean brilliance with a repetition rate suitable for different modes of photoemission detection. Together with the planned for 2021 source LCLS II this will make the European XFEL unique FEL facility for photoemission studies worldwide.

In this presentation an overview of time-resolved photoemission experiments on solids that were done at XFELs so far will be given and perspectives related to high repetition rate XFEL facilities, particularly European XFEL, will be provided.

4:40pm **SA+AS-MoA10 Revealing the Origins of Non-Joulian Magnetism with High-Resolution Photoemission Microscopy***, **Alexander Gray**, R.U. Chandrasena,* Department of Physics, Temple University*; H.D. Chopra,* Department of Mechanical Engineering, Temple University **INVITED**

All magnets elongate and contract anisotropically when placed in a magnetic field, an effect referred to as Joule magnetostriction. The hallmark of Joule magnetostriction is volume conservation, which is a broader definition applicable to self-accommodation of ferromagnetic, ferroelectric or ferroelastic domains in all functional materials. Recently, a new class of single-crystalline magnets exhibiting a 'giant' non-volume-conserving or non-Joulian magnetostriction was discovered [1]. In this talk I will discuss the results of our recent investigations of non-Joulian Fe$_3$Ga alloys using high-resolution polarization-dependent photoelectron microscopy. Our results suggest that non-Joulian magnetism arises from an unusual nearly-equipartition of the crystal into nm-scale lamellar domains and domain walls within highly periodic magnetic micro-cells. We suggest that this high-energy configuration is stabilized by the strain gradients arising from CDW that offsets electronic energy by a greater amount. High-resolution x-ray magnetic circular dichroism measurements at the Fe and Ga *L* absorption edges further provide evidence of weak iron-induced magnetism on gallium atoms via negative exchange. The results are in excellent agreement with the state-of-the-art theoretical electronic-structure calculations. Our findings open up new ways for the design of alloy systems having functional magnetic properties similar to Fe$_3$Ga where non-Joulian magnetostriction was first reported.

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Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 103C - Session SA+2D+AC+AS+TF-TuM

Applications of Synchrotron-based Techniques to 2D Materials (8:00-10:00 am)/Complex Functional Materials and Heterostructures (11:00 am-12:20 pm)

Moderators: Nicholas Barrett, CEA Saclay, Giacomo Ceccone, European Commission, Joint Research Centre, IHCP, Italy

8:20am **SA+2D+AC+AS+TF-TuM2 A Versatile Method for the Fabrication of 2D-electron Systems at Functional Oxide Surfaces***, T.C. Rödel,* Université Paris-Sud - SOLEIL, France*; **Patrick Le Fèvre,*** Synchrotron SOLEIL, France*; F. Fortuna, E. Frantzeskakis,* Université Paris-Sud - IN2P3, France*; F. Bertran,* Synchrotron SOLEIL, France*; T. Maroutian, P. Lecoeur,* Université Paris-Sud - CNRS, France*; B. Mersey,* Université de Caen, France*; A.F. Santander-Syro,* Université Paris-Sud - IN2P3, France

A critical challenge of modern materials science is to tailor novel states of matter suitable for future applications beyond semiconductor technology. In this prospect, 2D electron systems (2DESs), analogous to those created in semiconductors heterostructures, have been observed at the $LaAlO_3/SrTiO_3$ interface [1] and show amazing physical properties like metal-to-insulator transitions, superconductivity or magnetism. It was then demonstrated that 2DES could also be stabilized at the surface of $SrTiO_3$ [2] or other oxides [3], although it requires the use of intense UV or X-ray synchrotron radiation to desorb oxygen from the surface and dope it with electrons. This opened the way for the use of surface sensitive techniques, like Angle-Resolved PhotoEmission spectroscopy (ARPES) which provided a clear description of the microscopic electronic structure of the quantum well states. However, 2DESs at oxygen-deficient surfaces can be only manipulated and studied in ultra-high vacuum (to preserve the O-vacancies from re-oxidation) and thus, are not suited for experiments or applications at ambient conditions. Here we demonstrate a new, versatile and cost-effective method to generate passivated 2DESs on large areas of UHV-prepared functional oxide surfaces. It consists in a simple evaporation at room temperature of an aluminum film onto the oxide surface. Aluminum acts as a reducing agent and pumps oxygen from the substrate. It oxidizes into an insulating AlO_x layer, protecting an underlying homogeneous 2DES confined in the first atomic planes of the oxide substrate. 2 Å of Al are sufficient to create a saturated 2DES on differently oriented surfaces of $SrTiO_3$, anatase-TiO_2, or $BaTiO_3$, which were all studied by ARPES to determine the band structure (effective mass, orbital order and charge carrier densities) [4].

[1] A. Ohtomo, H. Y. Hwang, Nature **427**, 423 (2004).

[2] A. F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhes, R. Weht, X. G. Qiu, F. Bertran, A. Nicolaou, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthélémy, M. J. Rozenberg, Nature **469**, 189 (2011).

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[4] T. C. Rödel, F. Fortuna, S. Sengupta, E. Frantzeskakis, P. Le Fèvre, F. Bertran, B. Mercey, S. Matzen, G. Agnus, T. Maroutian, P. Lecœur, and A. F. Santander-Syro, Adv. Mater. **28**, 1976 (2016).

8:40am **SA+2D+AC+AS+TF-TuM3 Advanced Spectro-microscopy of Ion Irradiated Graphene-metal Interfaces: From Substitutional Implantation to Nanobubble Formation***, **Andrea Locatelli,** A. Sala, T.-O. Menteş,* Elettra - Sincrotrone Trieste, Italy*; G. Zamborlini,* Peter Grünberg Institute (PGI-6) Jülich*; L. Patera, C. Africh,* IOM-CNR Laboratorio TASC, Italy*; M. Imam, N. Stojić, N. Binggeli,* Abdus Salam International Centre for Theoretical Physics, Italy **INVITED**

The exploitation of graphene in the next generation electronics depends on our ability of preserving and tailoring its unique electronic and transport properties. Whereas the preservation of the free-standing characteristics of graphene demands to decouple the film from its support, their modification requires functionalization and thus chemical doping. Varied methods have been devised to implant exospecies into and under the C lattice mesh. Among them, irradiation of nitrogen ions has emerged as one of the most powerful approaches, producing enhanced physical and chemical properties rather than detrimental effects. At variance with other methods, ion irradiation enables implementation of lithographic approaches for doping graphene, a feature which is most desirable for creating arrays of devices.

The characterization of complex and laterally-heterogeneous interfaces, such as that of ion-irradiated graphene, demands advanced microscopy tools. Here, we will demonstrate the present capabilities of cathode lens spectro-microscopy. As a first example, we report a proof of principle experiment demonstrating that low energy ion irradiation through an aperture can be used to achieve local control on doping in graphene. Our study tackles the fabrication of a 2-dimensional heterojunction between *n*-doped and almost neutral single-layer graphene on Ir(111). Here, XPEEM is employed to characterize the transition region between areas with metallic and semimetal-like density of states and its thermal stability [1].

Then, we will focus on the irradiation of graphene with low energy Ar and Ne ions, reporting on the formation of nanobubbles upon annealing. The morphology and local stoichiometry of the Ar-ion irradiated interface were characterized by LEEM, XPEEM and STM, specifically addressing the thermal stability of noble gas nanobubbles. These structures display a lateral size up to tens of nanometers and height of several atomic layers. Remarkably, the Ar clusters remain trapped under graphene up to temperatures nearing 1100°C, suffering no material loss through the mesh or its edges. Ab-initio calculations demonstrate that intercalated Ar undergoes extreme pressures, up to few tens GPa. The nanobubble ripening process turns out to be driven by the minimization of the energy cost of film distortion and loss of adhesion [2]. The electronic properties of the ion irradiated interface will be also discussed.

[1] A. Sala, G. Zamborlini, T.O. Menteş, A. Locatelli; Small **11**(44), 5927–5931(2016).

[2] G. Zamborlini, M. Imam , L.L. Patera , T.O. Menteş , N. Stojić , C.Africh , A. Sala , N. Binggeli , G. Comelli and A.Locatelli; Nano Lett. **15**(9), 6162–6169 (2015).

9:20am **SA+2D+AC+AS+TF-TuM5 Gas-source MBE Growth of 2D Materials Examined using X-ray Synchrotron Radiation***, **Hugh Bullen,** R.K. Nahm, S. Vishwanath, H.G. Xing, J.R. Engstrom,* Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. Here we report on the gas-source MBE growth of thin films of WSe_2 using $W(CO)_6$ and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of $W(CO)_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence. We have examined growth for a variety of conditions: growth with coincident fluxes of $W(CO)_6$ and Se, and growth in which one of the two reactant fluxes was gated. These experiments were conducted at several different substrate temperatures, on graphite (HOPG), and on so-called epitaxial graphene (graphene on SiC). First, for continuous exposure to $W(CO)_6$ and Se we observe, after an short incubation period, continuous growth of both the W and Se intensities. Analysis of this data indicates a stoichiometry consistent with WSe_2. We also find diffraction features consistent with the crystalline phase of WSe_2, where the basal plane is in the plane of the substrate. Particularly interesting is what we see when one of the reactants is gated: We have found that growth is halted by gating the incident flux of $W(CO)_6$, while the film is stable in the presence of a flux of Se_n. The physical properties of these thin films are essentially the same as those grown using continuous exposure to both reactants. We find a much different result when the flux of Se_n is gated: the absence of Se, but the presence of $W(CO)_6$, leads to *loss* of Se, and an increase in the amount of W. Since the termination of both fluxes does not lead to the loss of either element, it must be that $W(CO)_6$ is providing the species that leads to the loss of Se. The most likely scenario is that a ligand exchange reaction occurs producing the gas phase species, SeCO(*g*). Perhaps our most exciting result involves the growth of WSe_2 on epitaxial graphene. In these experiments, in addition to measuring the X-ray fluorescence, we also measured *in situ* and in real time the intensity at the anti-Bragg condition, which we have shown to be are very effective way to monitor thin film crystal growth. We observe strong and sustained oscillations, indicating layer-by-layer growth of WSe_2 of up to at least 5 monolayers. This is a very exciting result, and it indicates the effective use of synchrotron radiation to examine the growth of TMD thin films.

9:40am **SA+2D+AC+AS+TF-TuM6 Nanostructured Surface of Multilayer Graphene on Cubic-SiC**, ***Victor Aristov,*** ISSP RAS, Chernogolovka, Russia, Russian Federation; *H.-C. Wu,* BIT, Beijing, China; *O.V. Molodtsova, S.V. Babenkov,* DESY, Hamburg, Germany; *A.N. Chaika,* ISSP RAS, Chernogolovka, Russia, Russian Federation

The results of atomically resolved scanning tunneling microscopy, low energy electron diffraction, low energy electron microscopy, micro-LEED and angle resolved photoelectron spectroscopy studies of graphene synthesized on cubic-SiC will be presented. Uniform few layer graphene was fabricated on SiC/Si wafers using Si-atom sublimation followed by SiC surface layer graphitization during high-temperature annealing in ultrahigh vacuum. Using the new dynamic-XPS end-station, based on the Argus spectrometer installed on the high-brilliance soft X-ray P04 beamline at PETRA III (DESY) one can control layer-by-layer graphene growth in real time following the evolution of the photoemission spectra with an acquisition time of ~ 0.1 sec/spectrum. Recording spectra during graphene growth on the SiC/Si(001) wafer, one can stop the process as soon as the desired number of graphene layers is reached. Angle-resolved photoemission measurements allowed us to extract the information about the electronic structure and the stacking order of the few-layer graphene on SiC(001). The preferential directions of the nanodomain boundaries coincide with the directions of carbon atomic chains on the SiC(001)-c(2x2) reconstruction, fabricated prior to graphene synthesis. Electrical measurements conducted on the vicinal SiC(001) samples demonstrate the opening of a transport gap in the nanostructured trilayer graphene. Our measurements demonstrate that the self-aligned periodic NBs can induce a charge transport gap up to 1.3 eV at low temperatures. The transport gap opening produces high current on-off ratio of 10^4. This development may lead to new tuneable electronic nanostructures made from graphene on cubic-SiC, opening up opportunities for a wide range of new applications.

This work was supported by the RAS, RFBR grants No 140200949 and 140201234, by the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211, by a Marie Curie IIF grant No 12/IA/1264, by SPP 1459 of DFG.

11:00am **SA+2D+AC+AS+TF-TuM10 Full-field Photoelectron Spectromicroscopy of Ferroelectric Surfaces**, ***Nicholas Barrett,*** CEA Saclay, France **INVITED**

Advanced low energy electron optics combined with synchrotron radiation has transformed photoelectron emission microscopy (PEEM) into a powerful technique for the microscopic study of material surfaces. High lateral, wave-vector and energy resolution makes it possible to probe spatial variations in the chemical and electronic structure of nanoscale materials.

Perovskite based ferroelectrics are one important family of oxide materials requiring such analysis. Their robust polarization, switchable by an external field, makes them extremely interesting candidates for post-CMOS electronics.

First, the principles of fully energy filtered PEEM will be presented. By a combination of both direct and reciprocal space imaging the surface charge, work function, topography, chemistry and band structure of ferroelectric materials can be studied. This will then be illustrated by several examples.

The surface charge and hence the ferroelectric polarization can be estimated from the the work function as measured in PEEM. There is a critical film thickness in $BiFeO_3$ below which the film polarization drops to zero despite constant tetragonality, suggesting the formation of stripe domains in ultra-thin films [1].

The band structure of ferroelectric domains in $BaTiO_3$(001) are studied using spatially resolved reciprocal space PEEM and synchrotron radiation. The dispersion relations can be correlated with domain chemistry and in- and out-of-plane ferrolectric polarization [2].

The ferroelectric stability as a function of temperature of piezo force microscopy written domains has been studied using threshold PEEM. A Curie temperature of 490°C is recorded which is also dependent on the poling voltage.

We will conclude with a brief demonstration of an operando PEEM experiment, opening up the perspective of studying the changes in functional oxide properties under electric stimulation.

[1] J. Rault, W. Ren, S. Prosandeev, S. Lisenkov, D. Sando, S. Fusil, M. Bibes, A. Barthélémy, L. Bellaiche and N. Barrett, Physical Review Letters 109, 267601 (2012)

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11:40am **SA+2D+AC+AS+TF-TuM12 Electron Confinement at Magnetic Oxide Interfaces: Insight from Photoemission Spectroscopy**, ***Martina Mueller,*** Forschungszentrum Juelich GmbH, Germany **INVITED**

Recent advances in the fabrication of oxide heterostructures with atomic-scale precision has enabled interface and size control of complex oxide materials, for which unique phenomena with no bulk analogues have been demonstrated. In designated heterostructures, two-dimensional electron systems can be confined at oxide interfaces -- typically along the growth direction – which offer possible alternatives to conventional semiconductors in terms of functional (e.g. spin-polarized) electronic transport properties. Using redox-controlled synthesis [1, 2], the electronic properties of oxide heterostructures and interfaces can be engineered -- in terms of quality that were thought to be unique to semiconductors.

The basic idea of electron confinement applies to complex oxides just as to conventional semiconductors, but the physics is much richer. In metal oxides, confined electrons are subject to strong electron-electron interactions leading to a variety of physical phenomena that can be accessed, modified and controlled. For example, using oxides with intrinsic magnetic order allows to explore spin-related phenomena in low dimensions.

We present how to create two-dimensional electronic systems (2DES) in all-oxide heterostructures using EuO, a ferromagnetic insulator [1]. By interfacing Eu metal to $SrTiO_3$, a non-magnetic insulator, a redox reaction takes place at the interface which involves the oxidation of Eu metal into ultrathin EuO [2], and the reduction of Ti cations. This redox process strongly suggests that mobile electrons are created at the resulting interface. Using synchrotron-based soft, hard and angle-resolved photoemission spectroscopy [3] we probe the electronic structure and chemical composition at the EuO/STO interface and give a direct indication of a redox-created 2DES. The observed electronic confinement in all-oxide heterostrctures provides a route for controlling spin functionality for emerging applications.

[1] G. Prinz, T. Gerber, A. Lorke, M. Müller, submitted (2016)

[2] T. Gerber, M. Müller *et al*, J. Mater. Chem. C, 4, 1813 (2016)

[3] M. Müller *et al*, J. Electron Spectrosc. Relat. Phenom. 208, 24 (2016)

Thin Film
Room 102B - Session TF+SA+MI-TuM
Thin Films for Synchrotron and Magnetism Applications

Moderators: Joshua Ballard, Zyvex Labs, Divine Kumah, North Carolina State University

8:00am **TF+SA+MI-TuM1 Achieving High-Temperature Ferromagnetic Topological Insulator by Proximity Coupling**, ***Valeria Lauter,*** Oak Ridge National Laboratory

Topological insulators (TIs) are insulating materials that poses conducting surface states protected by time-reversal symmetry, wherein electron spins are locked to their momentum. This exclusive property offers novel prospects for creating next-generation electronic and spintronic devices, including TI-based quantum computation. Introducing ferromagnetic order into a TI system without compromising its distinctive quantum coherent properties could lead to a realization of a number of innovative physical phenomena. In particular, achieving robust long-range magnetic order at the TI surface at specific locations without introducing spin scattering centers could open up new potentials for devices. Here, we demonstrate topologically enhanced interface magnetism by coupling a ferromagnetic insulator (FMI) to a TI (Bi_2Se_3); this interfacial ferromagnetism persists up to room temperature, even though the FMI (EuS) is known to order ferromagnetically only at low temperatures (< 17 K). The induced magnetism at the interface resulting from the large spin-orbit interaction and spin-momentum locking property of the TI surface is found to greatly enhance the magnetic ordering (Curie) temperature of the TI/FMI bilayer system. Due to the short range nature of the ferromagnetic exchange interaction, the time-reversal symmetry is broken only near the surface of a TI, while leaving its bulk states unaffected [1]. The topological magneto-electric response originating in such an engineered TI could allow for an efficient manipulation of the magnetization dynamics by an electric field, providing an energy efficient topological control mechanism for future spin-based technologies. Work supported by U.S. DOE, Office of Science, BES.

[1]F. Katmis, V. Lauter, F. Nogueira, B. Assaf, M. Jamer, P. Wei, B. Satpati, J. Freeland, I. Eremi[5], D. Heiman, P. Jarillo-Herrero, J. Moodera, "Achieving high-temperature ferromagnetic topological insulating phase by proximity coupling", *Nature 2016*

8:20am **TF+SA+MI-TuM2 Soft X-ray Induced Spin Crossover Transition at Room Temperature***, **Paulo Costa**, X. Zhang, S. Beniwal,* University of Nebraska-Lincoln*; A.T. N'Diaye,* Lawrence Berkeley National Laboratory*; J-F. Létard,* Université de Bordeaux*; P.A. Dowben, A. Enders,* University of Nebraska-Lincoln

The spin crossover Fe(II) complex (SCO) of the type [Fe(H$_2$B(pz)$_2$)$_2$(bipy)] has been previously shown to exhibit spin state transitions between its low spin (LS) and high spin (HS) states as a response to external stimulus such as electric fields, temperature changes, and light. It is well established that this SCO complex exhibits a crossover from its LS state to the HS state if the temperature is increased above approximately 150 K. It is demonstrated here that this spin crossover can be suppressed by mixing the SCO with strongly dipolar *p*-benzoquinonemonoimine zwitterion (PZI) molecules, so that unlike before, the LS state still prevails even at room temperature (RT). With the metastable LS state now locked in at RT, a spin state transition to the HS state can now be triggered optically by soft X-rays over a relatively short time of several minutes. This process is fully reversible, as cooling the mixture to 78 K has been shown to de-excite it back to its original LS state. Experiments were performed using X-ray absorption spectroscopy measurements (XAS) with synchrotron radiation tuned to the Fe L$_3$ absorption edge as well as accompanying magnetic moment measurements taken by a superconducting quantum interference device (SQUID). The effects of temperature, photon flux, and the stoichiometric ratio between SCO and PZI in the mixture were systematically studied, and the results will be presented here. This study provides a demonstration that the spin crossover transition temperature can be tailored to create a material that exists in a meta-stable LS state at RT wherein spin states can then be switched optically.

8:40am **TF+SA+MI-TuM3 Probing Thermochromic Phase Transitions in ALD VO$_2$ using Synchrotron Radiation***, **Alexander Kozen**,* U.S. Naval Research Laboratory*; H. Joress,* Cornell University*; V.D. Wheeler, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory

VO$_2$ is a thermochromic material, one class of "smart materials" that are receiving considerable interest due to a sharp semiconductor to metal (S-M) phase transition that occurs at a specific, material dependent temperature (T$_c$ = 68˚C for VO$_2$). The S-M transition occurs as a result of a phase transition between a semiconducting monoclinic phase below T$_c$ and a metallic tetragonal phase above T$_c$. While VO$_2$ has been widely utilized as a microbolometer material for IR detectors, current deposition processes used to fabricate thin film VO$_2$ (PLD, MBE, sputtering) are not adequate to realize complex device architectures. Use of ALD to deposit VO$_2$ thin films allows for uniform, low temperature coating of large area 3D substrates that could open the door to new applications.

Temperature dependent *in-situ* grazing incidence synchrotron XRD was utilized to probe lattice strain and structural reordering in both as-deposited (amorphous) and annealed (polycrystalline) ALD VO$_2$ thin films during the S-M transition. GIXRD allows us to selectively sample the bulk or the film-substrate interface of thin ALD films with excellent depth resolution, while the high flux provided by the synchrotron (10^{12} photons/s) enables fast data collection. Initial results show that as-deposited ALD VO$_2$ films are polycrystalline at the VO$_2$-sapphire interface, while the bulk of the as-deposited VO$_2$ is amorphous. Annealing VO$_2$ on sapphire in an oxygen-rich environment forms a fiber-textured polycrystalline VO$_2$ film with a more pronounced S-M transition. We will discuss how substrate selection, ALD growth and processing conditions, and film thickness influence VO$_2$ morphology and/or structure and relate these materials properties to device data.

The authors wish to acknowledge Cornell University's CHESS synchrotron facilities for GIXRD work and The Office of Naval Research for support. Dr. Kozen acknowledges support by the ASEE-NRL postdoctoral fellows program.

9:00am **TF+SA+MI-TuM4 Standing-wave Synchrotron Photoemission Studies of Electronic Structure in SrTiO$_3$-LaCrO$_3$ Superlattices***, **Ryan Comes**,* Auburn University*; S.C. Lin,* University of California, Davis*; C.T. Kuo,* Lawrence Berkeley National Laboratory (LBNL)*; L. Plucinski,* FZ Juelich*; S. Spurgeon,* Pacific Northwest National Laboratory*; D. Kepaptsoglou, Q. Ramasse,* SuperSTEM*; J.E. Rault,* Synchrotron SOLEIL*; S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; C. Fadley,* Lawrence Berkeley National Laboratory (LBNL)*; P.V. Sushko, S.A. Chambers,* Pacific Northwest National Laboratory

The polar discontinuity at the interface between SrTiO$_3$ (STO) and LaCrO$_3$ (LCO) has been shown to produce a varying band alignment between the two materials with a built-in potential gradient.[1] We have recently shown that this built-in potential gradient can be harnessed to induce a polarization in STO-LCO superlattices through interface engineering.[2] This work demonstrated that by controlling interfacial termination between layers we can induce a built-in polarization in STO, with Ti cations displaced off-center in surrounding oxygen octahedra. To further study this system, we have synthesized a series of STO-LCO superlattices with varying interfacial and surface terminations for synchrotron standing-wave x-ray photoemission measurements.[3] These measurements make use of Bragg diffraction from the superlattice to induce an x-ray standing wave that can be scanned across a single period of the superlattice. Through careful material design, we have achieved the strongest standing-wave effects to date, enabling angle-resolved photoemission measurements of electronic dispersion in both the STO and LCO layers of the material. Density functional theory models of the electronic structure of the superlattices are used to corroborate our experimental results with the expected behavior. Monochromated, aberration-corrected scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS) measurements also enable further studies into changes in electronic behavior at interfaces.

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9:20am **TF+SA+MI-TuM5 *In Situ* Synchrotron X-ray Studies of Complex Oxide Thin Film Growth***, **Dillon Fong**,* Argonne National Laboratory**INVITED**

Functional materials based on complex oxides in thin film form offer new and exciting strategies for meeting many of our outstanding energy challenges through systematic control of layer sequencing, strain, etc. However, the synthesis of such oxide films can be a major challenge even when utilizing reactive molecular-beam epitaxy (MBE), a powerful deposition technique that allows the construction of materials atomic plane by atomic plane. To understand the fundamental physics of oxide growth by reactive MBE, we present *in situ* surface x-ray diffraction results on the growth of SrTiO$_3$ and SrO-SrTiO$_3$ thin films on (001)-oriented SrTiO$_3$ substrates. For homoepitaxy, we compare sequential deposition (alternating Sr and Ti monolayer doses) with that of co-deposition of Sr and Ti, both in a background of oxygen pressure, and observe drastically different growth pathways due to the presence of a TiO$_2$ double layer. For heteroepitaxial growth of Ruddlesden-Popper SrO-SrTiO$_3$ films, we find that layers rearrange dynamically, resulting in layer sequences distinct from the shutter sequence. In general, the starting surface structure and composition, in combination with local thermodynamic considerations, strongly influence our ability to atomically construct new complex oxides.

Work at Argonne, including the Advanced Photon, is supported by the U.S. Department of Energy.

11:00am **TF+SA+MI-TuM10 Probing CVD Growth Mechanisms of SiC with *In Operando* Synchrotron-based X-ray Diagnostics***, **Philip DePond**, A.A. Martin, J.H. Yoo, M. Bagge-Hansen, J. Lee, S. Elhadj, M. Matthews, T. van Buuren,* Lawrence Livermore National Laboratory

Laser chemical vapor deposition (LCVD) of ultra-hard coatings, such as SiC, offers sub-mm spatial control over composition and phase, while addressing multiple growth processes under the same conditions for comparison. Normally, optimization requires extensive and costly "cook and look" experiments. Using an in situ approach instead, we develop fundamental insights into the growth mechanisms to unravel the complex roles of deposition parameters. We have conducted a series of in operando synchrotron-based X-ray absorption experiments that interrogate the LCVD growth region during growth. SiC was grown in a compact, portable CVD system from tetramethylsilane using a CW 532nm YAG to achieve laser-based pyrolytic precursor decomposition. We will present the results of Si K-edge (1.8keV) X-ray absorption near-edge structure (XANES) measurements conducted concurrently for the film during LCVD growth with an emphasis on the effects of variation of temperature, flow, substrates, and pressure conditions.

11:20am **TF+SA+MI-TuM11 Unusual Effects in Organic Thin Film Growth as Revealed by the Use of *In Situ* Real Time Synchrotron X-ray Techniques***, R.K. Nahm, H.J. Bullen, T. Suh, **James Engstrom**,* Cornell University

The effects of molecular scale events on the growth of crystalline thin films has been long been an active area of research as the resulting thin film properties depend sensitively on the microstructure. The growth of high quality, smooth thin films in the vast majority of these systems is favored at low rates of growth and high substrate temperatures. Here we report on the growth of thin films of tetracene, an organic semiconductor that possesses one less aromatic ring as compared to the much more studied pentacene. We examine the growth on SiO_2 using *in situ* real time X-ray synchrotron radiation and *ex situ* atomic force microscopy (AFM). First, using *in situ* X-ray reflectivity, we observe a transition from 3D island growth to 2D layer-by-layer growth as the growth rate of tetracene is *increased* on SiO_2 at room temperature, $T_s \sim 30$ °C. This unusual phenomenon, 2D growth favored at higher rates, has not been observed in previous work with pentacene, despite the similarities between these two molecules. Results from AFM indicate that tetracene may tend to quickly traverse "upwards" on thin film features such as the edges of islands, making these thin films susceptible to reorganization during and/or after growth. Thus, at sufficiently high rates of growth the rate of admolecule attachment at the tetracene island/SiO_2 substrate edges effectively outcompetes the rate of upward step-edge transport, and 2D growth results. We find additional evidence for this mechanism by examining the effect of substrate temperature. In particular we find that the transition to 2D growth occurs at a lower rate of growth at a substrate temperature of $T_s \sim 0$ °C, consistent with suppression in the rate of upward transport at lower values of T_s. Finally, we have also examined the evolution of the thin film crystal structure in real time using *in situ* grazing incidence X-ray diffraction. Many thin film organic semiconductors are known to crystallize in different structures, and tetracene is no exception. At room temperature we find that first a thin film phase grows, then, after a delay, a bulk phase begins to grow, while the growth of the thin film phase saturates. We also find that the film thickness at which X-ray scattering from the bulk phase becomes apparent is found to vary with deposition rate. These phenomena are also dependent on substrate temperature. For example, for the range of thin films thicknesses examined, we found no evidence for growth of the bulk phase at the lower substrate temperature, $T_s \sim 0$ °C. These results highlight the potential complexity of crystalline thin film growth in what appears to be a very simple system, tetracene on SiO_2.

11:40am **TF+SA+MI-TuM12 Understanding the Effect of Nitrogen Plasma on Plasma Assisted Atomic Layer Epitaxy of InN Monitored by Real Time GISAXS***, **Neeraj Nepal**, V. Anderson, S.D. Johnson, D.J. Meyer, B.P. Downey, A.C. Kozen,* US Naval Research Laboratory*; Z.R. Robinson,* SUNY College at Brockport*; D.R. Boris, S.C. Hernández, S.G. Walton,* US Naval Research Laboratory*; K.F. Ludwig,* Boston University*; C.R. Eddy, Jr.,* US Naval Research Laboratory

III-N semiconductors have found application in a variety of technologies such as high power transistors, emitters, detectors, and solar-cells. The relatively high growth temperature of common III-N synthesis techniques has impeded further development and application of the materials due to challenges with miscibility gaps and strain related to thermal expansion mismatch with non-native substrates. To address these challenges, Plasma assisted atomic layer epitaxy (PA-ALE) offers a new approach to low temperature III-N growth and can be used to epitaxially grow InN by using alternative pulses of trimethylindium and nitrogen plasma [1]. Since growth using this technique is far from thermodynamic equilibrium, understanding how nitrogen plasma affects nucleation and growth kinetics is essential for development.

Real-time grazing incidence small angle x-ray scattering (GISAXS) measurements at the Cornell High Energy Synchrotron Source were used to study the effect of variation in nitrogen plasma pulse conditions on PA-ALE of InN at 250 °C. Current results show the evolution of GISAXS characteristics such as the correlated peak (CP) length scale in the Yoneda Wing (YW) directly relates to the surface roughness, impurities, and electrical properties of the material. During the initial cycles of InN growth, the diffuse specular reflection broadens and CPs start to evolve along the YW with different correlated length scales. For the nitrogen plasma pulse time (t_p) of 15 seconds, the CPs have two different correlated length scales of 33.36 and 8.38 nm. With increasing t_p to ≥ 20s (the empirically optimal pulse length), a YW with only one CP evolves and the longest correlated length scale of 11.22 nm is for T_p = 25s. The correlated length scale of this single CP decreases to 10.75 nm for t_p = 30s. Additionally at t_p = 25s, the growth rate is largest (0.035nm/cycle – consistent with previously reported self-limited growth [1]) with root mean square surface roughness and carbon impurity at or below AFM and XPS sensitivity limits, respectively. The nature of GISAXS CP correlated length scale directly relates to the material quality. GISAXS also shows that the N_2/Ar flow ratio significantly affect the nucleation and growth of InN. Based on various *ex situ* characterization methods, the quality of the PA-ALE grown films is similar or better than the material grown by conventional growth methods, for example, molecular beam epitaxy at higher temperature (>400 °C).

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12:00pm **TF+SA+MI-TuM13 Spintronics Based on the Chiral Induced Spin Selectivity (CISS) Effect***, **Yossi Paltiel**,* The Hebrew University, Israel*; R. Naaman,* The Weizmann Institute of Science, Israel

The high level of energy dissipation associated with the present semiconductor-based integrated-circuit technology limits the operating frequency of the devices. Therefore there is interest in new concepts that may solve this problem. One such concept that attracts considerable attention nowadays combines spins with electronics (spintronics). In principle, the application of spintronics should result in reducing power consumption of electronic devices and efficiency should be closer to the thermodynamic limit.

Two major issues complicate the use of spintronics; material problems and the inefficiency in producing spin-polarized current. Spintronics devices usually require the use of complicated structures of magnetic material layers and the need for permanent magnetic layers puts constrains on the miniaturization of these devices. In addition, high currents are required to produce highly polarized spin current which results in induced heating.

We present a new concept in which spin current is produced by using the spin selectivity in electron transport through chiral molecules, termed Chiral-Induced Spin Selectivity (CISS). The CISS effect allows realization of simple local and power efficient spintronics devices. Studying the CISS effect, we found that chiral molecules, especially helical ones, can serve as very efficient spin filters at room temperature, with no need for a permanent magnetic layer. Recently, by utilizing this effect we demonstrated a simple magnetless spin based magnetic memory. Moreover, we show that when chiral molecules are adsorbed on the surface of thin ferromagnetic film, they induce magnetization perpendicular to the surface, without the application of current or external magnetic field.

The CISS-based spintronics technology has the potential to overcome the limitations of other magnetic-based memory technologies and to facilitate the fabrication of inexpensive, high-density memory and other spintronics elements.

Biomaterial Interfaces
Room 101A - Session BI+AS+SA-TuA

Biophysics and Characterization of Biological and Biomaterial Surfaces

Moderators: Eva Chi, University of New Mexico, Axel Rosenhahn, Ruhr-University Bochum, Germany

2:20pm **BI+AS+SA-TuA1 Resolving Non-specific and Specific Adhesive Interactions of Catechols at Solid/Liquid Interfaces at the Single Molecular Scale***, T. Utzig,* Max-Planck Institut für Eisenforschung GmbH, Germany*; P. Stock,* Max Planck Institut fur Eisenforschung GmbH, Germany*;* ***Markus Valtiner,*** Technische Universität Freiberg, Germany

The adhesive system of mussels evolved into a powerful and adaptive system with affinity to a wide range of surfaces. It is widely known that thereby 3,4-dihydroxyphenylalanine (Dopa) plays a central role. However underlying binding energies remain unknown at the single molecular scale. Here, we use single molecule force spectroscopy to estimate binding energies and binding mechanism of single catechols with a large range of opposing chemical functionalities. Our data demonstrates significant interactions of Dopa with all functionalities, yet most interactions fall within the medium-strong range of 10-20 k_BT. Specifically, Dopa-molecules interact with surfaces exposing different functionalities via different types of interactions ranging from bidentate H-bonding plus metal coordination (titania), monodentate H-bonding (SAMs exposing H-donor or H-acceptor headgroups), the hydrophobic interaction (alkyl SAM) or interactions involving the p-electron system of Dopa's catechol ring (gold). Only bi-dentate binding to TiO_2 surfaces exhibits a higher binding energy of 29 k_BT. Our data also demonstrates at the single molecule level that oxidized Dopa and amines exhibit interaction energies in the range of covalent bonds, confirming the important role of Dopa for cross-linking in the bulk mussel adhesive. We anticipate that our approach and data will further advance the understanding of biologic and technologic adhesives.

2:40pm **BI+AS+SA-TuA2 Protein-Nanoparticles Interactions: Surface Chemistry, Protein Corona and Secondary Structural Changes***, I. Ojea, R. Capomaccio, L. Calzolai, D. Gilliland, P. Colpo,* ***Giacomo Ceccone,*** EC-JRC-IHCP, Italy*; G. Siligardi, R. Hussein,* Diamond Light Source, Oxfordshire, UK

The characterisation of protein corona formed around nanoparticles is a very important and challenging issue in the investigation of nanomaterials behaviour in biological environment and has been studied by many authors [1, 2, 3,4].

On the other hand, it is recognized that detailed physico-chemical characterization of nanomaterials is becoming increasingly important both from the technological and from health and safety point of view. Moreover, an incomplete characterisation may inhibit or delay the scientific and technological impact of nanoscience and nanotechnology [5]. In this respect, surface chemical analysis methods, such as X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry, can provide an important contribution to more fully characterizing nanomaterials [6].

In this work, we have investigated the interaction of human serum albumin (HSA) with gold nanoparticles (AuNPs) functionalized with thiols. In particular, 15 nm AuNPs functionalized with PEG thiols have been studied before and after interaction with HSA.

The different steps of sample preparation have been characterised by DLS, CPS and TEM, whilst the surface chemistry has been mainly assessed by XPS. Finally, the interaction between nanoparticles and HSA has been studied by Synchrotron Radiation Circular Dichroism (SRCD) to gather information on the protein structure [7]. In particular, XPS and ToF-SIMS data revealed the presence of HSA on pegylated nanoparticles, whilst the use of SRCD in combination with separation techniques allowed the determination of the structure and morphology of HSA-AuNPs complexes [8]. Moreover, SRCD experiments indicate that AuNPs increase the UV and thermal stability of HSA.

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3:00pm **BI+AS+SA-TuA3 Measuring the Impact of the Surface of Protein Stability using Single Molecule Experiments with the AFM***,* ***Phil Williams,*** *S. Allen, A. Oyefeso, G. Milson, E. Fornari,* University of Nottingham, UK **INVITED**

Seven out of the top eight top-selling medicines of 2014 were biological in origin (so-called biopharmaceuticals or biologics). Successful formulation of such biopharmaceuticals has created new challenges to the pharmaceutical industry since the physical and chemical properties of the biological molecule (protein, peptide, RNA, DNA) differ from those of small 'classical drug' molecules. Whilst single molecule force spectroscopy has given new insight to many ligand/receptor interactions, the requirement to chemically functionalize the surfaces of both the substrate and the tip render the technique of little interest to the pharmaceutical industry since such functionalization, by definition, changes the chemistry of the ligand and receptor. Furthermore, this experimental methodology precludes effective screening of agents binding to a target receptor.

I will highlight our development of a fragment screening methodology using the AFM for single molecule force measurements without chemical modification of the ligands. I will introduce the method validating its approach using the streptavidin/biotin system that is often used as a model. I will then demonstrate the potential of the methodology to find fragments that interact with thrombin, a target for cardiovascular disease therapy.

In developing the above approach, it became apparent that actually neither the tip nor the substrate needs to be functionalized. I will conclude by discussing a promising method to screen for excipients that may stabilize protein structure in formulation and storage, where no chemical functionalization is necessary. The technique permits the measurement of the stability of proteins to be measured through their susceptibility to denaturants, such as urea and guanidinium chloride, and the effect of excipients on the measured stability to be assessed. For some proteins, the stability measured through traditional bulk methods, such as fluorescence, match those measured using the AFM, whereas for others there appears to be a significant difference. I propose, therefore, that this AFM method offers an interesting way to study protein denaturation at an interface.

4:20pm **BI+AS+SA-TuA7 In Vitro Characterization of Interfaces for the Development of Antibacterial and Biocompatible Surfaces***,* ***Katharina Maniura,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Cell culture and bacterial studies of novel materials and new functional surfaces often show very poor correlation with clinical outcomes. This fact not only poses a major challenge for basic and industrial researchers, it is also associated with high costs.

Generally, the majority of biomaterials are tested using *in vitro* cell monocultures, however, this approach neglects possible synergistic interactions between different cell types and paracrine signalling mediating the tissue-specific response to a material.

Immediately upon implantation, medical implants get exposed to the patient's blood and this initiates the first phase of wound healing and subsequent cell recruitment and response deciding about material integration or non-integration.

We have established that blood pre-incubation of implant surfaces mimics a more physiological situation, providing a more predictive *in vitro* model for the evaluation of novel implant surfaces.

Similarly, many promising antimicrobial materials failed to make the translation from bench to bedside, partially due to insufficient *in vitro* biofilm models used for predicting the long-term *in vivo* antimicrobial and anti-biofilm activity. For the evaluation of novel surfaces the actual forseen implantation location and its biological environment need be considered to design a more predictive bacterial study with conditions mimicking the *in vivo* situation.

5:00pm **BI+AS+SA-TuA9 Vibrational Sum-Frequency Scattering Spectroscopy for Characterization of Biomaterial Interfaces in Biological Environments***,* ***Patrik Johansson****, C. McDonald, Y.-C. Wang, P. Koelsch, D.G. Castner,* University of Washington

Most biomaterials have a 3-dimensional structure, of which the interfacial properties play an essential role in their interactions with biomolecules in the surrounding environment. The dynamics of protein adsorption onto biomaterials, and the induced conformational changes or selective orientations following such interactions, are phenomena that to a large extent govern the biocompatibility of such materials. However, direct measurement of these interactions in biological environments are challenging as most techniques often (1) lack interfacial specificity, (2) require model samples with inherent limitations, or (3) lack specificity for the chemistry, orientation, and conformation of the probed species. In this work, we demonstrate how vibrational sum-frequency scattering (SFS) can be used to provide all this information, without the use of labels, from biomolecules specifically at the surface of biomaterials in biological environments.

We first show that SFS can yield chemical information via vibrational spectra selectively from molecules used to functionalize the surface of nanoparticles. Spectral changes upon addition of proteins to the samples do not only confirm adsorption onto the nanoparticles, but also provide information about the secondary conformation for the adsorbed proteins. It is likely that continuous development of SFS will make it an essential tool for evaluating the biocompatibility and other properties of nanoparticles for use in biomedical applications.

We have also applied SFS on protein fibers, for which a detailed understanding of the structure, function, interactions, conformation, and dynamics is critical for refining strategies in tissue engineering, as well as for the development of treatments for progressive diseases involving protein fibers, such as Alzheimer's disease (AD). In our studies, we have found that collagen fibers assembled *in vitro* exhibit a very large SFS cross-section, and that the spectral signatures are dependent on the scattering angle, implying that this parameter can be adjusted to selectively study specific features of the fibers. Data analysis routines, including maximum entropy method calculations, reveal the relative phase of various chemical groups in the fibers, which can be utilized for determining their relative orientations.

Finally, we have demonstrated that amyloid fibers and spherulites, which are structures found in the brain tissue of patients with AD, exhibit strong nonlinear optical properties. We believe that SFS can reveal new details about the development and interactions of these structures, which can provide clues about AD pathology and help finding new biomarkers for the disease.

5:20pm **BI+AS+SA-TuA10 Imaging ToF-SIMS of Human Breast Cancer Tissues: Connecting Chemical Images to Biology*, Blake Bluestein,*** University of Washington*; F. Morrish, D. Hockenbery,* Fred Hutchinson Cancer Research Center*; L.J. Gamble,* University of Washington

Breast cancer, the most common cancer among women, is known to vary in responsiveness to chemotherapy. Therefore, the role of changes in tumor metabolism affecting the response to chemotherapy is under scrutiny. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) provides a powerful approach to attain spatially-resolved molecular data from cancerous tissues. We use imaging ToF-SIMS and principal components analysis (PCA) to study human biopsy tissue samples to clarify links between fatty acid composition within and around tumors and the potential drug resistance of these tumors. An important component of this project is ToF-SIMS analysis of pre and post neoadjuvant frozen patient specimens. Since treatment occurs with the tumor in place, analysis of biopsies taken pre- and post-treatment allows characterization of molecular changes in tumors as a response to treatment. Two sets of pre and post chemotherapeutic treated tissue have been studied. Additionally, 11 triple negative (TN) pre-treatment tissues have been studied using PCA to determine if molecular differences within tumor tissues can be correlated with patient response to treatment.

Data were acquired with an IONTOF TOF.SIMS V using a Bi_3^+ analysis beam. Multiple $1mm^2$ areas per tissue section were analyzed by stitching together 25 $200\mu m^2$ raster area scans. Data was acquired in both positive and negative polarities. Scores images generated by imaging PCA correlated with cellular and stromal areas were then used as masks to select regions of interest (ROI) that were reconstructed with ToF-SIMS software. Reconstructed spectral data of cellular and stromal areas was subsequently analyzed using PCA to ascertain molecular differences between tumor tissues.

Utilizing ROIs to select specific regions within analysis areas followed by spectral PCA for two different sets of pre and post treatment tumor biopsies showed a near distinctive chemical separation between pre and post. Chemical differences observed between the pre and post treatment tissue biopsies were related to changes in fatty acids, monoacylglycerols, diacylglycerols and cholesterol. Pretreatment samples showed higher loadings for vitamin E and C18:1 while post treatment samples had higher loadings for sphingomyelin and saturated fatty acids (stearic acid and palmitic acid). Spectral PCA of cellular and stromal region data from the 11 TN tissues separates patients that respond to chemotherapy and those that do not. Patients that respond to chemotherapy show higher loadings of sphingomyelin and saturated fatty acids, while nonresponding patients correlate with loadings of cholesterol, C18:1 and C18:2.

5:40pm **BI+AS+SA-TuA11 Some of These Images are Just Like the Others: Finding Similar Images in Imaging Mass Spectrometry Data Sets*, Daniel Graham,*** *L.J. Gamble,* University of Washington

Mass spectrometry imaging (MSI) has been applied to many areas of research due to the rich chemical information it can provide. However, MSI also brings a set of challenges due to the enormous size of the data sets. Most modern imaging mass spectrometers produce data that consists of a full mass spectrum at every pixel of each image. This data set can be analyzed either as a series of spectra from a given area of the image, or as a series of images from a given set of peak masses. When looking at a series images, it is of interest to find all masses that have the same spatial distribution since this could provide information about the chemical differences seen throughout a sample, and identify fragments that originate from the same molecules or that co-localize within the analyzed area. In this presentation we demonstrate a simple, useful tool we have developed to process mass spectrometry images and identify which peaks show similar spatial patterns. For this we have created the 'Correlated Image Finder' as part of our NBtoolbox for multivariate analysis of mass spectrometry imaging data. This tool uses one of two methods to find similar images. The first method calculates the correlation coefficient between the pixels of each image and sorts the images according to a user chosen correlation cutoff. The second method uses a simple image subtraction method to find images that match within a user chosen cutoff. For either method, the images are first down binned to reduce image noise and then thresholded and scaled in order to compare all peak images on an equal scale.

The Correlated Image Finder has been tested on a wide variety of images. Examples will be shown from ToF-SIMS and MALDI imaging data. It was seen that the Correlated Image Finder is able to find images showing similar spatial distributions. The Correlated Image Finder can be used on any set of image data and examples will be shown from both 2D and 3D image data sets from tissues, cells and polymers. The results from the Correlated Image Finder can help simplify MSI data interpretation and can also help understand trends seen using other analysis methods such as principal component analysis.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 103C - Session SA+AS+BI+MI-TuA

Synchrotron and XFEL Advances for Biological Systems (2:20-3:40 pm)/Synchrotron Radiation at the Frontiers of Device Technology (4:20-6:20 pm)

Moderators: David Shuh, Lawrence Berkeley National Laboratory, Olivier Renault, CEA-University Grenoble Alps, France

2:20pm **SA+AS+BI+MI-TuA1 Crystal Growth Mechanisms of Biominerals Revealed by Polarization-dependent Imaging Contrast (PIC) Mapping*, Pupa Gilbert,*** University of Wisconsin - Madison **INVITED**

X-ray linear dichroism was first shown in natural biominerals by Metzler et al. [1]. Based on this effect, we developed Polarization-dependent Imaging Contrast (PIC)-mapping, which displayed non-quantitative crystal orientation at the nanoscale as gray levels in ratios of images acquired at different linear polarizations [2]. A later development provided grayscale, semi-quantitative PIC-maps by acquiring stacks of 19 images as the linear polarization was rotated in 5° intervals from 0° to 90° [3-7]. The latest development uses the same stacks of images to fully, quantitatively display crystal orientations in colors, including hue and brightness, which represent in-plane and off-plane crystallographic c-axis orientation angles [8-10].

Using PIC-mapping in these 3 subsequent modes, we discovered several biomineral formation mechanisms in nacre [11,7], sea urchin teeth [12-14], ascidian spicules [10], corals, eggshells, modern and fossil sea shell ultrastructure [15].

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3:00pm **SA+AS+BI+MI-TuA3 New Dimensions in Synchrotron IR Spectroscopy*, Michael Martin,*** Lawrence Berkeley National Laboratory **INVITED**

Synchrotron infrared beamlines use the diffraction-limited beam properties to enable a variety of cutting edge science - how can we go further?

By combining scattering-scanning near-field optical microscopy (s-SNOM) with mid-infrared synchrotron radiation, synchrotron infrared nano-spectroscopy (SINS) enables molecular and phonon vibrational spectroscopic imaging, with rapid spectral acquisition, spanning the full mid-infrared (500-5000 cm^{-1}) region with nanoscale spatial resolution. This highly powerful combination provides access to a qualitatively new form of nano-chemometric analysis with the investigation of nanoscale, mesoscale, and surface phenomena that were previously impossible to study with IR techniques. We have installed a SINS end-station at Beamline 5.4 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, making the s-SNOM technique widely available to non-experts, such that it can be broadly applied to biological, surface chemistry, materials, or environmental science problems. We demonstrate the performance of synchrotron infrared nano-spectroscopy (SINS) on semiconductor, biomineral and protein nanostructures, providing vibrational chemical imaging with sub-zeptomole sensitivity.

The spatial field localization at the tip apex can also result in a large near-field momentum sufficient to optically excite phonon polaritons (PhPs), which are quasiparticles resulting from the strong coupling of photons with optical phonons. Here, we use SINS to image the PhP spectral response in thin hexagonal boron nitride (hBN) crystals. The large spectral bandwidth of the synchrotron source enables the simultaneous measurement of both the out-of-plane (780 cm-1) and in-plane (1370 cm-1) hBN phonon modes. In contrast to the strong and dispersive in-plane mode, the out-of-plane mode PhP response is weak. Measurements of the PhP wavelength reveal a proportional dependence on sample thickness for thin hBN flakes [2].

This talk will present the novel SINS instrumentation and a variety of scientific examples. Future directions, both technical and scientific, will be discussed.

*With Hans A Bechtel, Markus B. Raschke, Z. Shi, F. Wang, R.W. Johns, D.J. Miliron, E.A. Muller, R.L. Olmon

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4:20pm **SA+AS+BI+MI-TuA7 Sample Delivery Methods for X-ray Free Electron Lasers*, Uwe Weierstall,*** Arizona State University **INVITED**

Serial crystallography at XFEL's has shown great promise in recent years for solving crystal structures of proteins, which produce only micron sized crystals. Liquid jets have been very successful for delivery of microcrystals to the X-ray beam. The commonly used liquid injection system will be discussed. High sample consumption has motivated the development of an injector, which uses high viscosity media like Lipidic Cubic Phase (LCP). G-protein coupled receptors are an important group of membrane proteins which are often crystallized in LCP. The injector generations a microscopic stream of LCP with adjustable speed for sample delivery to the X-ray beam[1]. Some important GPCR structures could be solved with this device at the LCLS[2]. In addition, new media with similar viscosity to LCP have been developed which enable delivery of soluble or membrane proteins into the X-ray beam with low sample consumption[3]. The high viscosity injection method has also been shown to facilitate serial diffraction experiments with microcrystals at synchrotron microfocus beamlines. This talk will highlight these developments and discuss the possibilities.

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5:00pm **SA+AS+BI+MI-TuA9 Synchrotron-based Spectroscopy Investigation for Electronic Phase Transition at Highly-Charged Electric-Double-Layer Interfaces*, Hongtao Yuan,*** SLAC National Accelerator Laboratory **INVITED**

Electric-field control of charge carrier density has attracted much attention since it is remarkably simple for modulating physical properties of condensed matters and for exploring new functionalities with a transistor configuration. Owing to the limitation of dielectric breakdown in most solid dielectrics, the maximum carrier density accumulated in conventional field-effect transistors (FETs) is quite low (<< 10^{13} cm^{-2}) and thus seriously limits the tunability of electronic states of solids, for example, not sufficient enough to induce insulator-to-superconductor transition. While the electric-double-layer transistor (EDLT) with ionic liquids (ILs, or ionic gel) as gate dielectrics have been proved to be able to effectively attain a high carrier density up to levels of around 10^{15} cm^{-2} and to realize a large local electric field up to 50 MV/cm at liquid/solid interfaces. For example, electric-double-layer transistors have been demonstrated for an electric-field control of emergent interfacial quantum phenomena and the electronics phase transitions in condense matters, such as insulator-superconductivity and paramagnetism-ferromagnetism transitions. However, the mechanistic/spectropic understanding of the local electronic structures at such highly charged IL/oxide EDL interfaces and also further modification under gate-bias remain elucidated and challenging.

In this talk, we conducted synchrotron radiation based X-ray absorption spectroscopy (XAS) and Auger electron spectroscopy (AES) combined with in situ electrical measurements to directly characterize the evolution of the electronic structure at a representative IL/$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin film interface. We find a significant valence reduction localized to the topmost LSMO layer after interface formation, and that the gate-bias predominantly modulates this surface reduced Mn species effectively converting these top layers into an insulator. We expect the synchrotron radiation based photon science probing techniques will directly shed light on the understanding of interfacial electronic phase control under the electric field.

(This work was done in collaboration with Bongju Kim, Jun-Sik Lee, Yasuyuki Hikita adn Harold Y. Hwang. This work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under contract DE-AC02-76SF00515.)

5:40pm **SA+AS+BI+MI-TuA11 Correlation of the Conductivity/Magnetic Properties and the Electronic, Crystalline and Compositional Structure of Strongly Correlated Complex-oxide Interfaces and Thin Films***, **Juan Rubio-Zuazo,*** SpLine CRG Beamline at the ESRF The European Synchrotron, France*; G.R. Castro,* SpLIne CRG Beamline at the ESRF The European Synchrotron, France

We study the structural and electronic properties of strongly correlated complex-oxide thin films and interfaces using Hard X-ray Photoelectron Spectroscopy (HAXPES), Electron Energy Loss Spectroscopy (EELS) and Grazing Incidence X-ray diffraction (GIXRD) at the BM25-SpLine beamline (Branch B) at the ESRF. Strongly correlated complex-oxide exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. Usually, the interface drives the magnetic and electric response of the heterostructure. The chemical, mechanical, electric and magnetic properties of such devices are often intimately related to the structure, composition profile and morphology of their surface and internal interfaces. Several mechanisms are present at these interfaces as crystallographic space group modification, presence of oxygen vacancies, dislocations due to lattice strain, deviation from stoichiometry, phase segregation. In general all these phenomena modify the intrinsic properties of the materials used at the heterostructure, offering a unique way to produce artificial correlated materials with tailored properties. The growth of these materials in thin film form opens possibilities for magneto-electronic and spintronic devices applications. The results shown here are focused on the study of the influence of buried interfaces on the electric and magnetic properties of CMR and multiferroics systems. We will show the experimental methodologies at SpLine based on synchrotron radiation techniques to gain quantitative knowledge on the crystallographic and electronic properties at the interface between different complex oxides. There are few techniques able to provide an accurate insight of what is happening at these buried interfaces which in general are buried by several tens of nanometres in the material. The simultaneous combination of hard and soft X-ray photoelectron spectroscopy, electron energy loss spectroscopy with surface/interface X-ray diffraction gives unique capabilities in this respect. Here we will present a series of example to show how the interface properties can change the magnetic-conductivity properties.

6:00pm **SA+AS+BI+MI-TuA12 Interface Passivation of III-V/High-k Materials by High Energy X-ray Photoelectron Spectroscopy: A Quantitative Evaluation***, **Thierry Conard**, V. Spampinato, L. Nyns, S. Sioncke,* IMEC, Belgium*; J.M. Ablett,* Synchrotron SOLEIL- Ligne GALAXIES, France*; W. Vandervorst,* IMEC, KU Leuven, Belgium

The use of InGaAs as a high carrier mobility CMOS-channel material requires a proper electrical passivation of its interface with the gate dielectric. One of the passivation schemes investigated involves the use of Sulphur. In this work, high-k stacks on Sulphur passivated InGaAs substrates involving both Al2O3 and HfO2 are investigated. A major question related to the use of Sulphur relates to the chemical states at the interfaces. XPS is traditionally an important technique for interface analysis but faces several challenges in its application to the above mentioned stacks. First, due to the large number of elements involved, numerous peak interferences are present limiting the choice of useful photoemission peaks. Second, relevant stacks have total thicknesses of the order of 4 nm, which lead to very low intensities , certainly for minority elements like Sulfur. In this work, we discuss the impact of the H_2S passivation temperature as well as the use of TMA pre-pulses in the growth of Al_2O_3. We show that the Sulphur bind to In but that no As-S or Ga-S bonds could be detected. The use of a TMA pre-pulse after surface passivation leads to a reduction of the amount of Sulphur present at the interface and likely increases the amount of In-O bonds. Higher temperature H_2S passivation leads to a reduction of the amount of Sulphur at the surface.

We also observe that the presence/absence of S at the interface, as well as the presence of the Al_2O_3 buffer, which has a major impact on the relative peak position in the spectra between the substrate and the overlayer. This will be compared with the electrical characteristics of the stacks.

Finally, we show that using the Sessa software, full quantification of the stack can be obtained under the condition that all instrumental parameters are correctly taken into account.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room Hall D - Session SA-TuP

Novel Trends in Synchrotron and FEL-Based Analysis Poster Session

SA-TuP1 Transmission X-Ray Microscopy Characterization of PtNi Extended Surface Catalysts within MEAs for PEMFCs*, **Sarah Shulda**,* Colorado School of Mines*; J. Nelson Weker,* SLAC National Accelerator Laboratory*; C. Ngo,* Colorado School of Mines*; S. Mauger, K.C. Neyerlin, S. Alia, B. Pivovar,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

Proton exchange membrane fuel cells (PEMFCs) have a high power-to-weight ratio making them well suited for transportation applications. Platinum (Pt) nanoparticles on high surface area carbon is the current state of the art catalyst for the oxygen reduction reaction at the cathode. However, the high cost and inherent durability issues of this catalyst significantly limit the commercialization potential of PEMFCs in automobiles. Pt nanowires are a promising alternative to the carbon-supported Pt nanoparticles. High surface area platinum nickel (PtNi) nanowires have been synthesized and demonstrated exceptionally high activity and durability in electrochemical studies using rotating disk electrodes (RDEs). The incorporation of nanowire catalysts into full membrane electrode assemblies (MEAs) is not straightforward due to significant differences in the morphology of these materials as compared to traditional catalysts based on carbon-supported nanoparticles, and requires optimization of electrode composition and structure. Factors effecting the performance of the electrodes include catalyst content, amount of ionomer, amount and type of carbon additive, the three dimensional morphology of the nanowires, and nanowire contact with each other and with the other constituents of the MEA. In the specific case of NiPt nanowires, preventing Ni leaching is also imperative as Ni will poison the fuel cell and inevitably cause a significant drop in performance. Optimization of these parameters requires detailed understanding of the electrode structure, preferably using non-destructive techniques.

Transmission x-ray microscopy (TXM) allows for non-destructive three-dimensional analysis of full MEAs providing detailed information on electrode composition and structure. Ni and Pt are imaged separately through selective tuning of the incident x-ray energy, making their relative distribution throughout the MEA readily discernible. A series of MEAs with varying ink compositions was analyzed with TXM to study the effects of ionomer content, amount and type of carbon, and addition of poly(acrylic acid) (PAA) on electrode structure. MEAs pre-leached with acid to remove Ni were also imaged. Results demonstrated that ink formulations and acid leaching significantly impacted the nanowire morphology within the MEA. The addition of graphitized carbon nanofibers (GCNFs) resulted in more homogeneous and less densely packed nanowire distribution. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM) with energy dispersive elemental mapping complemented the TXM studies.

SA-TuP2 *In Operando* X-ray Imaging and Scattering from Detonating High Explosives*, M. Bagge-Hansen, M. Nielsen, L. Lauderbach, R. Hodgin, S. Bastea, L. Fried, D. Hansen, C. May, T. van Buuren, **Trevor Willey**,* Lawrence Livermore National Laboratory

The detonation of CHNO high explosives can generate an array of carbon nanomaterials including nano-onions, nano-diamond, and graphene products. The formation of these solid carbon phases occurs rapidly over the first several hundred nanoseconds, and a means to experimentally interrogate carbon nanomaterial formation during detonation will improve computational modeling and predictions of detonation phenomena. Experimental probes of carbon condensation under the extreme pressure and temperature conditions present during detonation at 100 ns timescales have been technically challenging to-date. Here, we present a new time-resolved small-angle x-ray scattering (SAXS) end-station, developed at LLNL and deployed at the Advanced Photon Source. This end-station at the Dynamic Compression Sector is capable of synchronously initiating detonation, and acquiring either small-angle x-ray scattering, or x-ray transmission radiographic images from discrete 80 ps x-ray pulses, which arrive every 153.4 ns during 24-bunch mode. The endstation can be trivially switched between SAXS and imaging modes. Images reveal densification within the explosive reaction zone, as well as detonation front curvature, and detonation velocity. The SAXS patterns demonstrate dramatic variation in the morphology and size of particles produced by different explosives. This work was performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344

Actinides and Rare Earths Focus Topic
Room 103C - Session AC+AS+SA-ThM

Chemistry and Physics of the Actinides and Rare Earths

Moderators: David Shuh, Lawrence Berkeley National Laboratory, Art Nelson, Lawrence Livermore National Laboratory

8:00am **AC+AS+SA-ThM1 Covalency in Oxidized Uranium*, James G. Tobin,*** University of Wisconsin-Oshkosh **INVITED**

Actinides, the 5*f* elements and their compounds, alloys, and mixtures, are a crucially important part of modern technological societies. Moreover, uranium dioxide is the most widely used nuclear fuel for the generation of electricity. Yet, because of the complexity of the 5*f*/6*d* electronic structure in the actinides, a fundamental understanding of their physical behavior, in actinides in general and uranium dioxide in particular, has not been achieved.

Theoretically, it has been proposed that covalency is an important part of the electronic structure of actinide dioxide, although some disagree. Experimentally, spectroscopic studies have been reported which support the hypothesis of 5*f* covalency. However, a crucially important and absolutely essential component has been missing: a systematic study where the nature of the oxidant is changed, so the specifics of the 5*f* and 6*d* covalencies could be varied and monitored. The turning-on and turning-off of an effect is the essence of a true benchmarking. The work reported here clearly and irrevocably establishes experimentally the strong presence of U 5*f* –O 2*p* covalency in the unoccupied density of states of UO2, the most important of our nuclear fuels.

This comparative study will feature the isoelectronic systems uranium dioxide (UO2) and uranium tetrafluoride (UF4). While isoelectronic, both being U^{+4} 5f^{2} in the formal limit, they exhibit substantially different structures. UO2 is a fluorite (cubic) material, while UF4 is monoclinic. However, both exhibit very similar U *L*3 extended x-ray absorption fine structure (EXAFS) behavior, indicative of quantitatively similar interatomic distances. The result of this comparative study is that UF4 exhibits continued 6*d* covalency but the almost complete loss of 5*f* covalency, while UO2 clearly displays both strong 5*f* and 6*d* covalencies. Here we have direct experimental demonstration that 5*f* covalency is important in actinide oxides but can be lost with a more powerful oxidizing agent such as fluorine.

To summarize: Using x-ray emission spectroscopy and absorption spectroscopy, it has been possible to directly access the states in the unoccupied conduction bands that are involved with 5*f* and 6*d* covalency in oxidized uranium. By varying the oxidizing agent, the degree of 5*f* covalency can be manipulated and monitored, clearly and irrevocably establishing the importance of 5*f* covalency in the electronic structure of the key nuclear fuel, uranium dioxide.

Collaborators on this work include: S.-W. Yu, R. Qiao, W. L. Yang, C. H. Booth, D. K. Shuh, A. M. Duffin, D. Sokaras, D. Nordlund, and T.-C. Weng. [*See PHYSICAL REVIEW B **92**, 045130 (2015)]

8:40am **AC+AS+SA-ThM3 An In Situ X-ray Diffraction Study of Plutonium Oxidation*, Paul Roussel,*** *W. Lake,* AWE, UK

X-ray diffraction was used to follow the oxidation of α-phase plutonium in oxygen at a pressure of 500 mbar. The composition of the growing oxide scale consisted of the trivalent cubic sesquioxide α-Pu_2O_3 and tetravalent fluorite dioxide PuO_2. The hexagonal β-sesquioxide phase was not detected. The quantity and lattice parameters of the oxide phases were determined from Rietveld analysis of the diffraction patterns. The lattice parameters of both oxides were found to decrease with increasing oxide quantity. Decreasing lattice parameters occur from increasing oxygen anion concentration in each oxide phase. The rate of oxidation for the total oxide composition at various temperatures below 100 °C was found to be linear, indicative of possible moisture enhanced oxidation. A detailed analysis of the contributions of the individual oxide compositions will be presented. Post oxidation optical microscopy of the coherent oxide scale showed areas of thicker scale typical of island growth. When the oxidation reaction was allowed to proceed to form olive green spalled oxide, X-ray diffraction analysis of the powder showed it to consist as a mixture of both cubic oxide phases.

Our initial XRD work presented at this meeting in 2012 suggested the initial oxide film grown on δ-plutonium might be amorphous. This work has been repeated using the XRD in-situ environmental reaction cell and the results will be presented.

9:00am **AC+AS+SA-ThM4 Advanced Applications of Synchrotron Sources to Describe Water Soluble Plutonium Colloids*, Thomas Dumas,*** CEA, France*; E. Dalodière, M. Virot,* ICSM Marcoule*; V. Morosini,* CEA Marcoule*; T. Chave,* ICSM Marcoule*; C. Hennig,* Helmholtz Zentrum Dresden-Rossendorf*; T. Wiss,* European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements*; D.K. Shuh, T. Tyliszcaak,* Lawrence Berkeley National Laboratory*; P. Moisy,* CEA Marcoule*; I. Nikitenko,* ICSM Marcoule

Colloidal species of Pu(IV) were shown to play a central role in the speciation of plutonium in various aqueous wastes and in biosphere [1-3]. However, a comprehensive understanding of the behavior and structure of Pu colloids remains elusive and hinders progress on the development of reliable processes of their management. Preparation of plutonium colloidal species with controlled composition and properties is still a challenge. Herein, we report the preparation of stable Pu(IV) colloids by the action of ultrasonic waves on PuO_2 in salt-free water conditions. Sonochemical colloid was compared with hydrolytic colloid using HRTEM, Pu LIII-edge EXFAS and STXM/NEXAFS techniques.

HRTEM revealed nanostructured morphology for both colloids composed of particles of PuO_2 (*fcc*, space group) measuring about 7 nm and 3 nm, respectively. The EXAFS spectra of colloidal PuO_2 nanoparticles were fitted on the basis of PuO_2 cristal structure. Combined HRTEM and EXAFS results revealed the correlation between the coordination numbers (i.e. Pu-O and Pu-Pu) and atomic surface-to-volume ratio of studied PuO_2 nanoparticles.

The STXM/NEXAFS technics implemented at ALS BL 11-0-2 was used for the first time to study plutonium colloids. It offers a new topographic angle to describe colloids combined to spectroscopic measurements at oxygen K edge. It first revealed that the oxygen state of hydrolytic Pu colloid is influenced by hydrolyzed Pu(IV) species in much more extend than the sonochemical colloids. Moreover the topographic analysis highlight discrepancies in plutonium and oxygen distribution for hydrolytic Pu colloid on the contrary to sonolitic one.

Complementarily to previous studies, this work confirmed that plutonium colloids (hydrolytic and sonochemical) can be described as core-shell nanoparticles composed of quasi stoichiometric PuO_2 core and hydrolyzed Pu(IV) moieties at the surface shell. Nevertheless, the application of soft X-ray technics highlight the strong influence of the synthetic route on colloid chemical composition and hence its expectable reactivity.

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9:20am **AC+AS+SA-ThM5 *In Pristinum* Observation of Plutonium Hydride*, Martin Brierley,*** *J.P. Knowles,* AWE

The reaction of plutonium with hydrogen creates plutonium hydride in an energetic process which often liberates the reaction product as a powder. Plutonium hydride is pyrophoric; therefore study of the reaction product usually requires that it is passivated by careful exposure to oxygen prior to removal from the reaction chamber. The passivation process is highly energetic with the potential to significantly affect the microstructure of the reaction product and surrounding metal. In this study we used a scanning electron microscope with an adjoining reaction chamber to maintain vacuum between reaction and analysis to grow plutonium hydride and subsequently analyse the reaction products as formed.

Initial work on electro refined Pu gave a slow reaction to hydrogen, requiring an *in situ* heat treatment to form hydride. Analysis of the reaction product was made *in vacuo* following reaction, preventing oxygen from accessing the sample. Subsequent cross sectional analysis of the reaction product morphology was performed, showing a coating of a hydride product layer with an open structure under the original surface oxide [1].

A sample of mixed α/δ phases was successively exposed to hydrogen for increasing durations of 60, 7200 and 70320 s. No evidence of reaction was evident following the 60 s and 7200 s exposures, unlike that observed in experiments on gadolinium [2] and uranium [3]. Following the 70320 s exposure, 96 % of the available hydrogen was consumed and several large anisotropic reaction sites had formed. The hydride sites on this mixed phase sample exhibited anisotropic growth similar to δ-stabilised plutonium samples investigated previously [4]. Deformation of the δ-phases surrounding hydride sites occurred via slip processes. Cracks formed in the overlying oxide layer above the deformed material allowing facile access for hydrogen to reach fresh Pu at the metal/oxide interface. Subsequent cross sectional analysis revealed anisotropic growth of hydride reaction sites, strongly supporting our previously proposed mechanism for anisotropic growth [4]. The α-phase domains resisted deformation and instead transferred the stresses from the hydride reaction front further into the surrounding metal. Post experimental cross sections through reaction sites suggest that hydride regions associated with α-domains had not undergone complete reaction.

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9:40am **AC+AS+SA-ThM6 Evidence for f- and d-orbital Mixing in Lanthanide and Actinide Dialuminides, MAl_2 (M = Ce, Sm, Eu, Yb, Lu, U, Pu)***, **Stefan Minasian**,* Lawrence Berkeley National Laboratory (LBNL)*; A.B. Altman, J. Arnold,* University of California at Berkeley*; E.D. Bauer,* Los Alamos National Laboratory*; C.H. Booth, J.I. Pacold, C.D. Pemmaraju, D.G. Prendergast, D.K. Shuh, T. Tyliszczak,* Lawrence Berkeley National Laboratory (LBNL)

For most scientific and technical applications, aluminum is well-regarded as a trivalent, electropositive and Lewis-acidic metal. However, this textbook model fails to adequately explain the unusual chemical and physical properties of many f-element molecules, materials, and alloys incorporating aluminum and other group 13 elements. In order to develop a more nuanced model of aluminum electronic structure, we have turned to metal K-edge X-ray Absorption Spectroscopy (XAS), which is an established technique for evaluating electronic structure in bioinorganic and inorganic compounds. Pre-edge peaks in K-edge XAS correspond to bound state transitions between core and unoccupied orbitals. Therefore, by comparing pre-edge features to established references, information can be gathered on the electronic structure of a system and the orbitals involved in bonding. However, there is very little precedent for the measurement and interpretation of aluminum K-edge XAS for molecules and materials.

This presentation will describe our recent efforts to develop Al K-edge XAS as a probe of chemical bonding and electronic structure in Al molecules and materials with lanthanide and actinide metals. Work began by examining a series of molecular aluminum compounds and by systematically varying supporting ligands and oxidation states. Features in the Al K-edge spectra were fully assigned through a comprehensive polarization study and comparison with the results of XCH and DFT calculations. Results were interpreted within a molecular orbital framework, providing unique insight that could not be obtained from analysis of NMR or metrics from single-crystal X-ray diffraction. These results have laid a foundation for ongoing efforts with lanthanide and actinide aluminum alloys, MAl_2 (M = Ce, Sm, Eu, Yb, Lu, U, and Pu). Comparisons between the Al K-edge spectra and earlier resonant X-ray emission spectra for the MAl_2 compounds provide unique insight into how electronic structure influences the desirable physical properties of these materials. For $EuAl_2$ and $YbAl_2$, the increasing occupancy of the 4f orbitals enhances screening of the 5d orbitals, resulting in enhanced Al 3p and Ln 5d orbital mixing for Eu and Yb that is not observed for Ce, Sm, or Lu. For UAl_2 and $PuAl_2$, the Al K-edge XAS and theory results also provides convincing evidence of Al 3p and 6d orbital mixing. Because of the enhance radial extension of the 6d orbitals, 6d orbital involvement in bonding for $PuAl_2$ is more likely to have an impact on the stability of the Pu–Al bonds. Current efforts are focused on evaluating f-element interactions with aluminum in other stoichiometric and non-stoichiometric alloys.

11:00am **AC+AS+SA-ThM10 Comparative Analysis of Uranium Oxide Films***, **Miguel Santiago Cordoba**,* Los Alamos National Laboratory

Depleted Uranium (DU) Oxide thin films are considered to be employed as surrogates and reference compounds for systematic studies on the elucidation of fundamental properties of actinide materials. The goal of this work is to compare surface morphologies of DU oxide thin films fabricated by two techniques, polymer assisted deposition (PAD) and electron beam evaporation (EBE). In this contribution, we utilized a MultiMode atomic force microscope (AFM) operating in tapping mode in order to compare and establish a contrast among the three dimensional surface structures of polycrystalline U_3O_8 and UO_2 films fabricated by PAD, and UO_2 thin films deposited by EBE. Differences in surface morphology are analyzed, and the information provided by AFM is compared against other complementary techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Reported results revealed that films fabricated by both techniques had granular structure, with morphologies strongly depending on the fabrication methods and conditions.

*Approved for public release LA-UR-16-22993

11:20am **AC+AS+SA-ThM11 Soft X-ray Spectroscopy of Actinide Materials***, **David Shuh**, S.G. Minasian, C. Pemmaraju, A. Canning, D.G. Prendergast,* Lawrence Berkeley National Laboratory*; T. Tyliszczak,* Lawrence Berkeley Lab, University of California, Berkeley*; A. Modin, S. Butorin, J. Nordgren, L. Werme, P. Oppeneer,* Uppsala University, Sweden

Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory to elucidate the electronic structure of actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of special-purpose actinide materials and the overall understanding of actinide materials. The experimental developments at the ALS have centered on the use of the Molecular Environmental Science (MES) scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and on X-ray emission spectroscopy (XES) at several beamlines, focusing primarily on light atom constituents (C, N, O, F) for ligand K-edge XAS, and on metal-ion centers plus light-atom signals for XES. The spectromicroscopy capabilities of the STXM provide the means to investigate and determine the speciation in actinide materials and environmentally-relevant systems with spatial resolution that reaches to the true nanoscale. An absolutely critical and key enabling component for all of the soft X-ray investigations is the contribution of theory, that when combined with experiment, has firmly provided more detailed knowledge of electronic structure in actinide materials in terms of orbital composition and mixing, and oxidation state.

Biomaterial Interfaces
Room 101A - Session BI+AS+SA-ThM

Synthesis and Processing of Biomaterials/Biologically Inspired Materials

Moderators: Daniel Barlow, US Naval Research Laboratory, Lara Gamble, University of Washington

8:00am **BI+AS+SA-ThM1 Response of PC 12 Cells to Mesoporous Substrates with and without DC Bias***, F. Sabri,* University of Memphis*; **Kyle Lynch**,* Universtiy of Memphis*; O. Skalli,* University of Memphis

The interaction of nerve cells with nanostructured surfaces and substrates is of great importance to the field of tissue engineering and artificial substrates developed for biomedical applications. It has been established that cells respond to different polymer surface characteristics such as roughness, surface free energy, topography, chemistry, charge, and other properties including electrical conductivity. It has also been recognized that the nanotopography can affect and influence cell morphology, cell alignment, cell signaling and extension of neurites. Here, we discuss the influence of the mesoporous structure of crosslinked silica aerogels on the adhesion, proliferation, and neurite extension of PC 12 cells, in the presence and absence of applied DC bias. The behavior of cultured PC 12cells on the aerogel substrates is compared to the behavior of cells cultured on cell culture plastic (control) and the affect of applied DC bias of different magnitudes is carefully investigated. The neurite extensions clearly show a preferred growth direction and the rate of growth of extensions is also influenced by the varying conditions.

8:20am **BI+AS+SA-ThM2 Collagen Functionalized with ALD-TiO_2: A Novel Biomaterial for Bone Grafting***, **ArghyaKamal Bishal**, C. Sukotjo, C.G. Takoudis,* University of Illinois at Chicago

In medicine, the use of implants is growing rapidly. Some patients may not have enough bone to support such implants.[1, 2] Therefore, those patients are required to have augmentation, a procedure to increase the height or width of inserted bone-like supporting materials, prior to implantation.[1] Collagen resorbable membrane is used as a bone grafting material which acts as supporting material and facilitates new bone formation.[3] Sometimes, titanium reinforced collagen membrane is used for improved stability.[2]

Collagen is an important biomaterial which is used in several biomedical applications. It has a triple helix structure made of polypeptide chains.[3, 4] Hydrogen bonds play an important role in keeping together these peptide chains. Glycine, proline are the most abundant amino acids found in its structure. Collagen has also the ability to be reorganized and crosslinked and thus turn into flexible fibrils with higher tensile strength.[3]There are four main types of collagen: type I, II, III and V. Among them mostly type I and little amount of type V construct the bone structure by forming a composite with hydroxyapatite (HA) crystals.[4]

Titania (TiO_2) itself is biocompatible.[5] Additionally, it has the ability to attract Calcium and Phosphate in a liquid environment.[6] Therefore TiO_2 coated collagen may be used as an excellent bone grafting material to nucleate Ca and P and thus reconstructing a stable bone structure. In this work, we present ALD of TiO_2 on collagen membrane in a custom-made ALD reactor. The deposition was performed at room temperature. Tetrakis(dimethylamido)titanium (TDMAT) and ozone were used as metal precursor and oxidizer, respectively. Samples were characterized for their surface morphology, composition and mechanical properties. Energy dispersive spectroscopy confirmed the presence of Ti on coated collagen and electron microscopy showed an increase in fiber diameter after deposition by more than a factor of 2:

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8:40am **BI+AS+SA-ThM3 Nanostructure Formation on Biomaterials by Directed Irradiation Synthesis (DIS) for Tissue Regeneration and Maximize Corrosion Resistance***, Jean Paul Allain,* *A.R. Shetty,* University of Illinois at Urbana-Champaign*; S. Arias, A. Barnwell,* University of Illinois at Urbana Champaign*; F. Echeverria, L.F. Berrio,* University of Antioquia, Colombia

An important aspect of tissue engineering is to create a favorable extracellular microenvironment, mainly the extracellular matrix (ECM) which can guide cell differentiation and tissue regeneration. The ECM consists of a number of cues that can be guided by surface topography and matrix stiffness [1]. Recent studies [2,3] have demonstrated that depending on the type of surface structuring and patterning, cell adhesion can be controlled with potential applications in smart cell culture systems and biosensors. Many of the desired biomaterial properties that require a combination of metal alloy and soft material interfaces cannot be processed with conventional bottom-up techniques. Directed irradiation synthesis (DIS) address this limitation by introducing a synthesis process that is scalable to high-volume manufacturing by virtue of its intrinsic large-area simultaneous exposure of materials surfaces and interfaces.

In this study, we have employed directed irradiation synthesis to induce nanostructure formation on two commonly used biomaterials: 1) Ti_6Al_4V and 2) magnesium (Mg). The goal is to examine the role of surface nanostructuring on the stimulation of cells and tissues in order to provide important cues for tissue regeneration as well as guarantee a good corrosion resistance and to minimize bacteria adhesion. Detailed characterization, establishing processing conditions and correlating them to surface and biomaterial properties have been successfully performed on nanostructured medical grade Ti_6Al_4V and Mg. These irradiated surfaces were biologically evaluated by using human aortic smooth muscle cells (HASMCs) for cytotoxicity and cell/surface adhesion and interactions. This analysis allowed us to determine connections with processing, structure, surface energy, and biointerface properties. Biological response of these new surfaces has also lead us, for the first time, to establish correlations between nanostructuring by DIS and cell stimulation, as well as to show the real potential of these new surfaces to favorably stimulate cells and tissues different than bone. The corrosion behavior of these biomaterials in a phosphate buffered simulated body fluid (SBF) has also been investigated for bone implant application.

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9:00am **BI+AS+SA-ThM4 Controlled Peptide Surfaces of Various Ratios that Guide Neural Stem Cell Differentiation***, HalaShakib Dhowre,* *M. Zelzer, H. Sahaf, C. Towlson, N.A. Russell,* University of Nottingham, UK

Cell instructive biointerfaces represent an essential aspect for the advancement of regenerative medicine. Currently, a major issue in biointerface design is the limited ability to mimic the complex interactions of the natural processes in the extracellular matrix (ECM) with artificially designed surfaces and interfaces [1]. While biomaterial surfaces have been shown to be able to elicit specific cell responses (e.g. adhesion, proliferation, differentiation), precise control akin to that of natural cellular environments is still lacking[2].

AIM:

The present work aims to address this challenge by designing new synthetic peptide surfaces with well controlled composition and functionality able to impact control over the differentiation of neuronal stem cells with the ultimate goal to understand and control how neuronal networks function.

METHODS:

Compositionally well defined surface concentrations of two short laminin peptide sequences, Arg-Gly-Asp (RGD) and Ile-Lys-Val-Ala-Val (IKVAV) were prepared of various ratios via the "grafting from" stepwise approach and the surface modification was confirmed with surface analysis techniques to indicate successful peptide functionalisation. The neural stem and progenitor cells (NSPC) were set up from embryonic rat hippocampi (E18). Immunocytochemistry (ICC) observed cell viability and differentiation to specific NSPC lineages for Nestin, βIII-Tubulin and GFAP.

RESULTS:

Surface characterising techniques (WCA, AFM and ToF-SIMS) verified the successful amino acid build-up to peptides on the surfaces, allowing modification of the surfaces with RGD and IKVAV. Enhanced NSPC adhesion, proliferation and differentiation were observed on the peptide surfaces. ICC demonstrated Nestin expression decrease after the removal of the growth factors (EGF and FGF) and an increase in the expression of βIII-Tubulin and GFAP; thus illustrating cells differentiating from stem cells to neurons or astrocytes due to peptide surface influence.

CONCLUSION:

Well defined peptide surfaces were designed successfully, the various ratios of RGD and IKVAV surfaces demonstrated cell adhesion, proliferation and i desirable effects in controlling different populations of stem cell fate. These surfaces may advance new insight in understanding how surface properties affect the regulation of physiological relevance in directing neural cell differentiation, which will be essential to understand how neural networks function.

References

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9:20am **BI+AS+SA-ThM5 Biofunctional Hydrogels for Tissue Repair***, Andres Garcia,* Georgia Institute of Technology **INVITED**

Hydrogels, highly hydrated cross-linked polymer networks, have emerged as powerful synthetic analogs of extracellular matrices for basic cell studies as well as promising biomaterials for regenerative medicine applications. A critical advantage of these synthetic matrices over natural networks is that bioactive functionalities, such as cell adhesive sequences and growth factors, can be incorporated in precise densities while the substrate mechanical properties are independently controlled. We have engineered poly(ethylene glycol) [PEG]-maleimide hydrogels to study epithelial morphogenesis and identified independent contributions of biophysical and biochemical properties of these materials to this developmental process. In another application, we have developed synthetic hydrogels that support improved pancreatic islet engraftment, vascularization and function in diabetic models. These studies establish these biofunctional hydrogels as promising platforms for basic science studies and biomaterial carriers for cell delivery, engraftment and enhanced tissue repair.

11:00am **BI+AS+SA-ThM10 Nanoscale Domain Formation Induced by Partial Polymerization Creates Planar Supported Lipid Bilayers that are Fluid and Stable***, **N.Malithi Fonseka**, B. Liang, K.S. Orosz, C.A. Aspinwall, S.S. Saavedra,* University of Arizona

Planar supported lipid bilayers (PSLBs) are widely explored bilayer platforms for receptor-based biosensors. PSLBs composed of fluid lipids lack the stability necessary for many technological applications due to the relatively weak non-covalent interactions between lipid molecules. Lipid polymerization enhances bilayer stability, but may greatly reduces lipid mobility and membrane fluidity. In an effort to enhance bilayer stability while maintaining fluidity, we have prepared and characterized PSLBs composed of mixtures of the polymerizable lipid bis-Sorbyl phosphatidylcholine (bis-SorbPC), and the fluid lipid diphytanoyl phosphatidylcholine (DPhPC) to form mixed PSLBs. We measured lateral diffusion coefficients (*D*) as a function of the bis-SorbPC/DPhPC molar ratio using fluorescence recovery after photobleaching (FRAP). In pure DPhPC PSLBs, *D* = 0.66 μm^2/sec. In equimolar poly(bis-SorbPC)/DPhPC, *D* = 0.36 μm^2/sec, whereas when the ratio is greater than 0.7, *D* decreased to 0.13 μm^2/sec. These data show that considerable fluidity is retained even when the poly(bis-SorbPC) fraction is substantial, which suggests that these bilayers are phase segregated, composed of polymerized and fluid domains. However domains were not observed with fluorescence microscopy techniques. The sub-µm morphology of these PSLBs was therefore investigated using atomic force microscopy (AFM). Nano-scale phase segregation of the two lipids was observed. DPhPC forms a continuous lipid matrix that is 0.2-0.4 nm thicker than the island-like poly(bis-SorbPC) domains. This height difference agrees with bilayer thicknesses measured for pure DPhPC and poly(bis-SorbPC) PSLBs. Furthermore, it was observed that the size of the poly(bis-SorbPC) domains increased with the percentage of poly(bis-SorbPC) in the PSLB. In summary, mixed lipid bilayers composed of poly(bis-SorbPC) and DPhPC form nano-structured membranes with retained lipid diffusivity, and thus they have considerable potential for creating membrane-based biosensors in which receptor activity depends on bilayer fluidity.

11:20am **BI+AS+SA-ThM11 Stabilization of Lipid Films by Hyaluronic Acid and Polymeric Substitutes in a Joint Model System***, **Felicitas Schwoerer**,* Universität Heidelberg, Germany*; M. Trapp, R. Steitz,* Helmholtz-Zentrum Berlin für Materialien und Energie GmbH*; R. Dahint,* Universität Heidelberg

In the United States there are 27 million people suffering from osteoarthritis. The disease is primarily caused by the degeneration of cartilage, which covers the bone ends of the joints and is in turn decorated with a phospholipid (PL) layer. The bone ends are separated by the synovial fluid containing the polysaccharide hyaluronic acid (HA) as a main component. It is generally assumed that both HA and PLs reduce friction and protect the cartilage. Based on the observation that HA concentration is reduced in diseased joints, a new cure called viscosupplementation has been developed, where HA or mixtures of HA and PLs are injected into the joints. However, until now the positive effect of such therapy is under debate.

To elucidate the importance of HA and PLs for joint lubrication and protection on a molecular level we investigate their interaction using a simplified model system for natural joints. A silicon wafer (representing the bone end) is covered with PL oligobilayers and incubated in an aqueous solution containing HA or polymeric substitutes (representing the synovial fluid). To mimic the forces in joint movement, we expose the model surfaces to a home-built shear apparatus facilitating *in situ* measurements at a rotational speed between 0 rpm and 6000 rpm. Measurements were performed at *BioRef* (Helmholtz-Zentrum Berlin), a time-of-flight neutron reflectometer with integrated infrared spectroscopy.

Upon contact with both HA and poly(allylamine hydrochloride) (PAH) solutions a tremendous swelling of the lipid film occurs. Film thickness increases by a factor of about four compared to pure D_2O exposure due to a drastic increase in the thickness of the interstitial water layers located between adjacent lipid bilayers. This effect is most likely due to the adsorption of charged polymers at the lipid headgroups leading to electrostatic repulsion. Despite their high film thickness and water content, the polymer-exposed lipid films exhibit approximately ten times higher shear stability than the respective systems incubated in pure water. With increasing rotational speed the lipid films contain substantially enhanced water fractions, which we attribute to increasing lateral fragmentation. Present investigations aim at the question whether HA and PAH are incorporated into the lipid tail region and bridge adjacent bilayers as this might explain the observed higher stability.

11:40am **BI+AS+SA-ThM12 New Substrates and Patterning Methods for Supported Lipid Bilayers***, **Sally McArthur**, L. Askew,* Swinburne University of Technology, Australia **INVITED**

The cell membrane encases and protects cellular components and plays an important role in transport, signalling and disease. Studying membrane behaviour is a challenging task due to the complexity and scale on which these processes occur. Supported lipid bilayers (SLBs) have provided researchers with stable and reproducible platforms to recreate cell membrane environments. The planar structure of the model means a variety of patterning techniques can be employed to recreate membrane architecture on both a micro and nanoscale. In particular, pre-patterned substrates are of great interest as they eliminate complications associated with preserving membrane integrity during patterning. Plasma polymers provide a versatile method of creating thin films with a variety of different surface chemistries. In this work we explore the behaviour of plasma coatings in aqueous conditions and the use of plasma films for creating patterned SLBs using vesicle collapse. The results demonstrate that variations in plasma polymer chemistry can be used to control lipid bilayer formation and the locations of different lipid species. Characterisation of film behaviour and bilayer formation was conducted using a variety of techniques including ellipsometry, quartz crystal microbalance with dissipation (QCM-D), confocal microscopy, atomic force microscopy (AFM) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

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