Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 9 - Session SA+MI-TuM
Overcoming the Temporal and Spatial Limits of X-Ray Scattering Methods for In-Situ Analysis

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

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

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

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

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

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

In particular, it is challenging to detect the complex morphologies, which are necessary to have high efficiency organic solar cells. The combination of grazing incidence small and wide angle x-ray scattering (GISAXS and GIWAXS) allows for overcoming these challenges.[1-4] The crystalline structure is probed with GIWAXS and the mesoscale structure is determined with GISAXS. Based on selected examples, the impact of different layers in the functional stack build-up of organic solar cells,[5,6] in-situ studies during printing[7] and in-operando studies of organic solar cells[8] are presented.

References

[1] M.A.Ruderer, P.Müller-Buschbaum; Soft Matter **7**, 5482-5493 (2011)

[2] P.Müller-Buschbaum; Adv. Mater. **26**, 7692-7709 (2014)

[3] A.Hexemer, P.Müller-Buschbaum; IUCrJ **2**, 106-125 (2015)

[4] P.Müller-Buschbaum; Polymer Journal (invited review) **45**, 34-42 (2013)

[5] S.Guo, M.A.Ruderer, M.Rawolle, V.Körstgens, C.Birkenstock, J.Perlich, P.Müller-Buschbaum; ACS Appl. Mater. Interfaces **5**, 8581-8590 (2013)

[6] W.Wang, S.Pröller, M.A.Niedermeier, V.Körstgens, M.Philipp, B.Su, S.Yu, S.V.Roth, P.Müller-Buschbaum; ACS Appl. Mater. Interfaces **7**, 602-610 (2015)

[7] C.M.Palumbiny, F.Liu, T.P.Russell, A.Hexemer, C.Wang, P.Müller-Buschbaum; Adv. Mater. **27**, 3391-3397 (2015)

[8] C.J.Schaffer, C.M.Palumbiny, M.A.Niedermeier, C.Jendrzejewski, G.Santoro, S.V.Roth, P.Müller-Buschbaum; Adv. Mater. **25**, 6760-6764 (2013)

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

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

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

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

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

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

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

Gold clusters grown on 10 ML MgO(100)/Mo(100) are investigated as a model system for using static XUV photoemission as a probe of electronic character versus cluster size. As the size of the Au clusters is increased, a gradual shift in the photoemission onset up to the Fermi energy indicates a change in the character of the gold clusters from non-metallic to metallic. The results are compared with theoretical work and previous investigations to validate the XUV-PES method. Static photoemission is then further utilized to monitor the electronic structure of Zn clusters on p–Si(100) as a function of Zn deposition. The transition from non-metallic to metallic Zn character is observed at 0.16 ML of Zn coverage. Furthermore, the femtosecond pump-probe XUV-PES technique is employed to induce a charge transfer from the p-Si(100) substrate to the Zn clusters and to measure in real time the charge trapping at the Zn clusters as well as the subsequent charge relaxation. The ultrafast charge carrier dynamics investigations are performed as the Zn dimensionality is increased from small clusters composed of a very few atoms to large collections of atoms to extended Zn films.

12:00pm **SA+MI-TuM-13 Direct Observation of TiO_2 Exciton Recombination***, **Geoff Thornton**,* Universty College London, UK*; Y Zhang, D Payne, C Pang,* University College London, UK*; C Cacho, R Chapman, E Springate,* STFC Rutherford Appleton Laboratory, UK

Exciton recombination pathways are of paramount importance in photocatalysis because they determine the lifetime of the chemically active electrons and holes, and hence the catalytic efficiency. These pathways are not known in detail even for a prototypical material such as TiO_2, where the related process of electron trapping is important in a broader range of applications (eg resistive switching). Here we use time-resolved femtosecond pump-probe photoemission spectroscopy (TRPES) to investigate exciton recombination and electron trapping in a state resolved fashion. This employed an XUV probe following an infra-red or UV pump. When an infra-red pump is employed, electrons in polaronic band gap states (BGS) are excited to the bottom of the conduction band. The subsequent recapture time of 50±10 fs is determined by directly monitoring the intensity change of the BGS and hot electrons in TRPES spectra. When a UV pump is employed, electrons are excited either from the BGS to a resonance in the CB, or from the top of the valence band (VB) to the bottom of the CB. The same trapping of hot electrons is observed as for infra-red excitation. In addition, a long lifetime component (>1 ps) of the hot electron decay and the BGS recovery are observed, pointing to trap assisted exciton recombination.

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