Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic
Room B116 - Session LX+AS+HC+SS-MoM

Laboratory-Based AP-XPS: Advances in Instrumentation and Applications

Moderators: Sylwia Ptasinska, University of Notre Dame, **Heath Kersell**, Oregon State University

8:20am **LX+AS+HC+SS-MoM-1 Instrumentation for Electron Microscopy and Spectroscopy in Plasma Environment***, **Andrei Kolmakov,*** NIST-Gaithersburg **INVITED**

Plasma-assisted processes are of principal importance for modern semiconductors microfabrication technology, catalysis, environmental remediation, medicine, etc. Understanding the chemical and morphological evolutions of the surfaces and interfaces under a plasma environment requires *operando* metrologies that have a high spatial, temporal, and spectroscopic resolution. Combining the APXPS system with ambient pressure scanning electron microscopy would, in principle, meet these needs. Here we review the status of the field and discuss the prospective designs as well as application examples of ambient pressure scanning electron microscopy and spectroscopy for *in situ* analysis and processing of the surfaces under plasma environments

9:00am **LX+AS+HC+SS-MoM-3 Scienta Omicron HiPPLab - A Lab-based APXPS Instrument for Probing Surface Chemical Reactions***, **Peter Amann,*** Scienta Omicron, Germany

Investigating reaction intermediates, oxidation states, solid-liquid interfaces and buried interfaces under near ambient pressure conditions is highly desired in materials science applications. Ambient pressure X-ray photoelectron spectroscopy (APXPS) is a powerful method to investigate the chemical nature of surfaces and interfaces and has undergone a tremendous improvement in the last years. The development of the HiPP analysers allowed to overcome the one bar pressure regime without using pressure separating membranes. [1] [2]

During the past decade, increased attention has been shown to laboratory based APXPS system solutions, which is motivated by the 24/7 access capability and possibility for highly customized sample environments. Drawing on extensive experience in the fields of photoelectron spectroscopy, UHV technology, and system design, Scienta Omicron has designed the HiPPLab as an easy-to-use system that encourages user creativity through flexibility, modularity and an innovate chamber design.[3] It combines a state-of-the-art HiPP analyser with a high flux, variable focus X-ray source. Multiple options complement the HiPPLab offer, including a gas reaction cell, a preparation chamber, laser heating, or options for mass-spectroscopy. Using automated gas-flow controllers, experiments can be conducted in a controlled way. Future upgrade possibilities are given.

The HiPP-3 analyser features a 2D detector allowing for spatial resolved measurements with customer proven results down to 2.8 µm resolution. The swift acceleration mode allows for high electron transmission without applying a sample bias. A sophisticated pre-lens design in which efficient pumping between two close-by apertures is implemented, allows dragging out corrosive gases or moisture, which would otherwise be detrimental to the instrument.

In this presentation, I will give an overview on our APXPS product portfolio focusing on laboratory based solutions and present application examples.

[1] Amann, et al. *Review of Scientific Instruments*, 2019 *90*(10)

[2] Takagi, et al. X-ray photoelectron spectroscopy under real ambient pressure conditions. *Applied Physics Express*, 2017, *10*(7), 8–11.

[3] Scienta Omicron HiPPLab https://scientaomicron.com/en

9:20am **LX+AS+HC+SS-MoM-4 Using Microheaters for Time-Resolved APXPS and Correlated ETEM***, **Ashley Head,*** Brookhaven National Laboratory*; B. Karagoz,* Diamond Light Source, UK*; J. Carpena-Nuñez,* Air Force Research Laboratory*; D. Zakharov,* Brookhaven National Laboratory*; B. Maruyuma,* Air Force Research Laboratory*; D. Stacchiola,* Brookhaven National Laboratory

With a rise in the number of lab-based APXPS systems, these instruments afford an opportunity to continue the development of multimodal and correlated capabilities for more comprehensive information of reactions at surfaces. Here I will discuss the methods of using an ETEM commercial microheater for collecting APXPS data on the same sample under identical conditions. A specialized holder was fabricated to use commercial microheaters on MEMS chips in a lab-based APXPS instrument. The rapid heating of the microheater enables a time-zero for collecting APXPS data with a time resolution of 500 ms. Proof-of-principle measurements following the oxidation and reduction of a Pd film demonstrate correlative experiments with TEM. The specialized holder was fabricated with the possibility of dosing gases locally to the sample surface while confined by a graphene membrane. Using the gas lines, the Pd film was oxidized under a partial pressure of air (~0.4 mbar). Overall, using this microheater in APXPS offers chemical information complementary to structural changes seen in ETEM. The rapid heating enables new opportunities in time-resolution and increased pressure for APXPS experiments.

9:40am **LX+AS+HC+SS-MoM-5 NAP-XPS Instrumentation Came a Long Way - Where Will Applications Lead Us from Here?***, P. Dietrich, F. Mirabella, K. Kunze, O. Schaff, **Andreas Thissen,*** SPECS Surface Nano Analysis GmbH, Germany **INVITED**

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into the most important standard surface analytical method in many laboratories for surface and materials characterization.

For the last fifteen years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention. Although invented as a laboratory method it initially started to grow at synchrotrons. The development of more efficient and sensitive electron analyzers and high-brilliance monochromated laboratory X-ray and UV sources running at pressures of up to 100 mbar finally brought it back to the individual laboratories. The reasons are the availability of individual infrastructure for sample preparation and handling, safety regulations and easier access to measurement time on a daily basis. Nowadays the vast majority of instruments worldwide are laboratory-based.

It opened the method XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces and many more. The development of instrumentation followed the important applications and besides the "active" components, mainly excitation sources and electron analyzers, a lot of developments have been done in the fields of sample environments, sample handling, system setup and automation and combination with other techniques and even in quantification of data. There are only a few applications left where experiments at synchrotron based beamlines and end stations offer the only solution.

The market driving applications nowadays are catalysis, electrochemistry, behaviour of liquid phases, biological samples and surface chemistry. Along these applications this presentation will show the existing instrumentation, discuss its limits and the perspective for near future developments to further increase the user base of laboratory based NAP-XPS systems to turn it into an integral part of the large routine analysis community.

10:40am **LX+AS+HC+SS-MoM-8 Evolution of Metal-Organic Frameworks in the Presence of a Plasma by AP-XPS and IRRAS***, **J. Anibal Boscoboinik**,* Brookhaven National Laboratory and State University of New York at Stony Brook*; M. Ahmad,* Stony Brook University/Brookhaven National Laboratory*; M. Dorneles de Mello,* Brookhaven National Laboratory*; D. Lee,* Johns Hopkins University*; P. Dimitrakellis,* University of Delaware*; Y. Miao,* Johns Hopkins University*; W. Zheng,* University of Delaware*; D. Nykypanchuk,* Brookhaven National Laboratory*; D. Vlachos,* University of Delaware*; M. Tsapatsis,* Johns Hopkins University **INVITED**

Zeolitic imidazolate frameworks (ZIF), a class of metal-organic frameworks, are promising materials for various applications, including the separation and trapping of molecules and catalysis. Recent work has shown that exposure to plasma can result in the functionalization of the framework for tailored applications. This talk will report in-situ plasma studies of ZIF-8 as a model system. We will study the framework's evolution in the presence of N_2, O_2, and H_2 plasmas by combining lab-based ambient pressure XPS and infrared reflection absorption spectroscopy.

11:20am **LX+AS+HC+SS-MoM-10 Surface Degradation and Passivation in Perovskite Solar Cells***, **Wendy Flavell,*** The University of Manchester, UK **INVITED**

There is an urgent requirement to make better use of the 120,000 TW of power provided by the Sun, by using it to generate power, or by using its energy directly to make useful chemical feedstocks. Around the world, there is an explosion of research activity in new systems for harvesting solar energy, including solar cells based organometal halide perovskites. Issues of key importance are the interfacial energy level line-up of the cell components, and the influence of the surface properties of these materials on charge separation in the devices. Indeed, the deployment of perovskites in solar cells is currently limited by their high reactivity and rate of surface oxidation. Thus, a key problem is to develop an understanding of the interface chemistry of solar heterojunctions in order to develop passivation strategies. I show how a combination of techniques including near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and hard X-ray photoelectron spectroscopy (HAXPES) may be used to investigate surface ageing and the surface degradation reactions[1-7], chemical composition as a function of depth[4,5], and to develop passivation strategies for perovskite solar cell heterojunctions[2,3,5-7].

References

1. J C-R Ke, A S Walton, A G Thomas, D J Lewis, *et al.*, *Chem Commun* **53**, 5231 (2017).
2. J C-R Ke, D J Lewis, A S Walton, B F Spencer, *et al.*, *J Mater Chem A*, **6**, 11205 (2018).
3. C-R Ke, D J Lewis, A S Walton, Q Chen, *et al., ACS Applied Energy Materials* **2**, 6012 (2019).
4. B F Spencer, S Maniyarasu, B P Reed, D J H Cant *et al.*, *Applied Surface Science* **541**, 148635 (2021).
5. S Maniyarasu, J C-R Ke, B F Spencer, A S Walton *et al.,ACS Applied Energy Materials* **13**, 43573 (2021).
6. S Maniyarasu, B F Spencer, H Mo, A S Walton *et al.*, *J Mater Chem A*, **10**, 18206 (2022).
7. D Zhao, T A Flavell, F Aljuaid, S Edmondson*et al., ACS Applied Materials and Interfaces,* submitted.

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