

Thin Films and Surface Modification

Room Naupaka Salon 4 - Session TF2-MoE

Thin Films - Characterization

Moderator: Chen-Hao Wang, National Taiwan University of Science and Technology

7:40pm **TF2-MoE-7 In-Situ/Operando Soft X-Ray Measurements for Hydrogen Related Surface Functional Materials, Ryo Toyoshima**, The University of Tokyo, Japan **INVITED**

Chemical reactions at surfaces have been widely used for chemical processes such as catalytic synthesis, energy conversion, environmental cleanup, and sensor. Surface science techniques enable us to understand physicochemical fundamental processes on surfaces. However, one drawback of such surface science techniques is that the experiments are carried out under vacuum in many cases. We have developed some in situ / operando experimental techniques for observing surface reactions on liquid/solid and gas/solid interfaces in energy range from infrared to soft X-ray. We have focused on the development and understanding of heterogeneous catalysts using hydrogen gas as a reducing agent [1], and sensing materials to detect small molecules such as hydrogen [2], by ambient pressure X-ray photoelectron spectroscopy (AP-XPS). The experiments were carried out at a beamline BL-13 at the Photon-Factory of High Energy Accelerator Research Organization (KEK-PF). The AP-XPS system is consisted of a high-pressure chamber, preparation chamber and load-lock chamber. An important technical point of the AP-XPS system is that the high-pressure chamber, where quasi-atmospheric gases are introduced, and the electron analyzer are separated by a small aperture and pumped by a differential pumping system. It keeps the pressure of electron analyzer under ultra-high vacuum, and it also reduces the scattering of photoelectrons in the gas atmosphere. Recently, a sensor material has been developed that can detect H₂ gas in air and breath with high sensitivity (1 ppm) using nanometer-thick platinum-based thin films [2]. Figure 1 shows a result of operando AP-XPS measurement for H₂ sensing Pt-Rh thin-film sensor. The Pt-Rh sensor detects the atmospheric concentration of H₂ gas by changing in electric resistivity. Here, a 10 nm-thick Pt-Rh thin-film deposited on a SiO₂ substrate was used for the measurements. Figure 1(a) shows time evolution of relative electric resistivity ($\Delta R/R$). The resistivity decreases with exposing H₂ gas to the sensor surface, whereas it increases with exposing O₂ gas. Figure 1(b) shows corresponding Rh 3d and Pt 4f XPS. Before the gas dosing (i), the surface was dominated by Rh oxide. When the surface was exposed to the H₂ gas, the chemical state clearly changed. The Rh oxide was completely reduced to the metallic state. When, the surface was exposed to the O₂ gas, the oxygen-induced species grew up again. Those findings indicate the surface chemical state strongly relate to the material functions.

[1] Toyoshima, R. et al. J. Phys. Chem. C 2021, 125, 4540–4549.

[2] Toyoshima, R. et al. J. Phys. Chem. Lett. 2022, 13, 8546–8552.

8:20pm **TF2-MoE-9 NAP HAXPES from Tender X-Ray Energies, Paul Dietrich**, SPECS Surface Nano Analysis GmbH, Germany

X-ray photoelectron spectroscopy (XPS) is a powerful technique for investigating a wide range of materials' chemical composition and electronic structure. The information depth of XPS is contingent upon the inelastic mean free path (IMFP) of the photoelectrons in solid matter. The IMFP as a function of kinetic energy exhibits a pronounced minimum at kinetic electron energies between 40 and 100 eV. The maximum kinetic energy of photoelectrons in an XPS experiment depends on photon energy. In this context, typical photon energies employed in laboratory settings and at synchrotron radiation facilities range up to 1500 eV. In such experiments, the inelastic mean free path is typically around a few nanometers making conventional XPS a surface-sensitive technique. It is necessary to increase the kinetic energy of electrons by using higher photon energies for excitation to gain access to properties at the bulk and interface levels. In hard X-ray photoelectron spectroscopy (HAXPES), photon energies typically range between 3 keV and 15 keV, thereby extending the information depth to 10–30 nm.

The μ FOCUS 450 is a versatile small-spot multi-wavelength X-ray monochromator for surface analysis and depth profiling applications. This fully computer-controlled device allows for in situ switching between different emitters for Al, Ag, and Cr excitation, thus providing X-rays with high flux density for various applications such as small, medium, and high energy XPS. This new monochromator is an all-in-one solution for (NAP)

XPS and (NAP) HAXPES systems. It combines the high performance of the standard aluminum Ka excitation (1487 eV) with silver La and chromium Ka excitation lines at 2984 eV and 5414 eV, respectively. The new design hosts up to three anodes and the corresponding monochromator optics in one Rowland circle based housing.

Due to signal absorption in the surrounding gas, NAP XPS is one of the most challenging applications in surface analysis. High-performance analyzers, such as the AEOLOS 150 NAP, require a matched X-ray source, fitting the small analyzer field of view and the need for a high flux density on the smallest spots. The μ FOCUS 450 is designed to cover these requirements for highly efficient NAP XPS and NAP HAXPES measurements. The combination of our monochromatic three-color X-ray source μ FOCUS 450 with Al, Ag, and Cr anodes together with the high transmission hemispherical analyzer AEOLOS 150 NAP is ideally suited for studies of interfaces under reactive conditions extending the information depth from the surface into the bulk. We will present a selection of recent (NAP) HAXPES results from different types of samples.

8:40pm **TF2-MoE-10 Redox XPS; Progressive *proxime situ* Oxidation in XPS (and SIMS) as an Aid to Spectrum Interpretation, Peter Cumpson**, La Trobe University, Australia; *D. Devadasan*, Thermo Fisher Scientific, UK; *S. Gazzola*, University of Bath, U.K.; *T. Nunney*, Thermo Fisher Scientific, UK; *R. Weatherup*, Oxford University, UK

We have developed a method of exposing surface analysis samples to a progressive series of oxidation steps in the entry-lock of a UHV instrument (e.g. ThermoFisher K-Alpha and NEXSA XPS instruments). Shortwave UV and part-per-million ozone are used in automated steps to progressively oxidise specimens so that one obtains a series of narrow-scan XPS spectra representing increasingly oxidised states. This makes it easier to interpret the superposition of chemical states that existed in the original spectrum of an "as received" specimen, and indeed, to numerically extract spectra representing the pure components. This is not done *in situ* in the analyser, or *ex situ* outside the instrument, but rather *proxime situ* in the entry lock without having to take the sample out of the instrument. This allows Redox XPS to be done automatically and unattended, rather like a depth-profile. To be clear, this is not done to study the chemistry of UV or ozone exposure, but just to elucidate the chemical components of the specimen surface before that exposure.

After a brief review of the experimental arrangement we present a comprehensive analysis of spectral unmixing in Redox XPS, focusing on the treatment of spectra in the presence of the inelastic background. The study introduces novel approaches for analyzing narrowscan XPS spectra of progressively oxidized samples, offering significant insights into the decomposition of complex spectral data into its constituent chemical states. By leveraging advanced computational techniques, this approach significantly improves the accuracy and reliability of chemical state identification in XPS analysis, and should address some of the important issues raised in the community recently regarding the reliability of peak-fitting performed by those new to XPS.

This progressive gas-phase oxidation offers even more opportunities in the understanding of SIMS spectra, given the more specific ozonolysis chemistry of complex organics. We look at the opportunities (with data - if we have it by December).

Author Index

Bold page numbers indicate presenter

— C —

Cumpson, P.: TF2-MoE-10, **1**

— D —

Devadasan, D.: TF2-MoE-10, **1**

Dietrich, P.: TF2-MoE-9, **1**

— G —

Gazzola, S.: TF2-MoE-10, **1**

— N —

Nunney, T.: TF2-MoE-10, **1**

— T —

Toyoshima, R.: TF2-MoE-7, **1**

— W —

Weatherup, R.: TF2-MoE-10, **1**