

1. Status of Beamline BL07LSU at SPring-8

The University-of-Tokyo high-brilliance synchrotron soft X-ray outstation beamline BL07LSU at SPring-8 has been maintained by the permanent staff members with adjuncts for user operations. A scientific aim of the beamline is to promote advanced spectroscopy for solid state and soft (including bio) materials. There are four regular endstations: time-resolved soft X-ray spectroscopy (TR-SX spectroscopy), soft X-ray diffraction, 3D-scanning photoelectron microscope (3D nano-ESCA) and ultrahigh resolution soft X-ray emission spectroscopy (HORNET) that are open for users. There is also a free port station for users who bring their own experimental apparatus. In 2018, we have completed commissioning of the ambient pressure X-ray photoelectron spectroscopy station at the free port station and opened the system for general users.

The beamline BL07LSU is equipped with a segmented cross-type undulator. By using phase shifter among the undulator segments, a polarization control of soft X-ray was started since 2016. Circularly and linearly polarized soft X-rays at full energy range (250 – 2000 eV) have been available by tuning the permanent magnet type phase shifter. In 2018, we have introduced a soft X-ray chopper that can transmit only a selected pulse of the incident beam in order to improve signal to noise ratio of specific experiments like time-resolved spectroscopy of slow dynamics, operando spectroscopy under applied bias or to reduce radiation induced damages.

At the beamline endstations, various scientific researches were carried out by both the laboratory staffs and general users (G-type application). Below are brief introduction of recent activities at each station.

(1) Time-Resolved soft X-ray spectroscopy station (TR-SX spectroscopy)

The station is to perform time-resolved photoemission spectroscopy experiments by synchronizing the high-brilliant soft X-ray and the ultra-short laser pulses. A two-dimensional angle-resolved time-of-flight (ARTOF) analyzer has been equipped for the efficient time-resolved measurements and the measurement temperature can be controlled from 15 K to 1150K. The station adopts two different optical laser systems synchronized with synchrotron soft X-ray; low repetition rate and high pulse energy (1 kHz, mJ) and high repetition rate and low pulse energy (208 kHz, μ J). In addition, an optical parametric amplifier (OPA) has been installed for both laser systems to cover a wider spectrum range of optical laser.

In 2018, time-resolved photoelectron diffraction experiments were performed on a monatomic two-dimensional layer of Si, Silicene. Two-dimensional detection of

photoelectron diffraction patterns and a chemical shift in high energy resolution measurements by ARTOF allow us to trace temporal evolution of Si atom positions in a site-specific manner.

Photo-excited carrier dynamics in a model organic photovoltaic system was studied using time-resolved soft X-ray photoelectron spectroscopy. Monolayer-thick *p*-type metal phthalocyanine (CuPc) and *n*-type fullerene (C₆₀) layers were deposited on a TiO₂(110) surface. Electrons excited in the unoccupied states of CuPc and C₆₀ are swiftly transferred to the conduction band of TiO₂ substrate, leaving the molecules in transient cationic states. The cationic states have long lifetime of the order of microseconds, suggesting that an electron-hole recombination is efficiently suppressed at the organic/TiO₂ interface.

(2) 3D-scanning photoelectron microscope (3D nano-ESCA)

3D-nano-ESCA can be used for sub-100 nm range microscopic 2D mapping and depth profile of the chemical structure of functional materials and devices.

In 2018, we have devised new technique enabling to probe the electronics states of buried interfaces of GaN-HEMT in academia-industry collaboration with Sumitomo Electric Industries, by combining 3D nano-ESCA with advanced device technologies. This work was published in Scientific Reports in 2018. As a joint research with Dr. Asakura and Dr. Hosono at AIST group, we also combined 3D nano-ESCA with optical microscope images, and studied Li ion diffusion mechanism in a μm sized SnO₂ wire and local Li insertion/extraction process in a Li₄Ti₅O₁₂ (LTO) negative electrode active material under operando (electrochemically operating) condition. The result on LTO was published in Journal of Electron Spectroscopy and Related Phenomena. As collaboration with Department of Materials Engineering, the University of Tokyo, we performed operando nano-spectroscopy on device structures of transition metal dichalcogenide tunnel field effect transistors (TMD-TFETs) and found difference in gate and drain voltage dependence of the potential distribution between MoS₂ on highly- and low- doped p⁺-WSe₂. Furthermore, we also conducted academia-industry collaboration research on process-induced defects in SiC trench MOSFETs based on the previous results published in e-JSSNT in 2018.

(3) Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)

This station allows *Operando* observation of catalysts under reaction conditions using AP-XPS. The AP-XPS station was constructed in 2014 by an external funding (JST ACT-C project), and was opened to external users in 2018.

The AP-XPS system is equipped with a differentially pumped electron analyzer

(SPECS, PHOIBOS 150 NAP) and an ambient-pressure gas cell. XPS measurements can be performed both under ultrahigh vacuum and in near-ambient gas pressure up to 20 mbar. Catalytic activity is monitored by mass spectrometer, and simultaneous evaluation of adsorbate and catalyst electronic states is performed by AP-XPS. In addition to the experiments at the free port station using synchrotron soft X-ray, off-line experiments using a twin-anode X-ray source can be performed.

A variety of research projects are now in progress at the AP-XPS station: (i) Methanol synthesis on Cu-Zn catalysts, (ii) Sabatier reaction on Ni catalysts, (iii) H₂ adsorption/absorption in Pd nanoparticles and Pd alloys (PdAg and PdCu), (iv) CH₄ partial oxidation on Pd catalysts, (v) CO₂ adsorption on graphene support, (vi) band alignment at a semiconductor photoelectrode and electrolyte interface, (vii) development of time-resolved AP-XPS.

(4) Ultra high-resolution soft X-ray emission spectroscopy (HORNET)

The station is dedicated for soft X-ray emission (or resonant inelastic X-ray scattering: RIXS) spectroscopy measurements with ultrahigh-resolution ($E/\Delta E > 10,000$) and under various environmental conditions (gas, liquid, and solid). The number of applications to the HORNET station is increasing. In 2018, we have performed 15 collaborative research using the HORNET station: two S-type proposals, five proposals for molecular systems, four for condensed matter physics, and four for electrochemistry of batteries. In molecular systems, the behavior of water in a variety of circumstances was studied, such as water around disaccharide, water at the interface of biocompatible polymers, and hydration to plasma treated carbon nanotube and boron nitride. Jet system was installed in order to discuss pure vibrational spectra without the contribution from an X-ray filter. In condensed matter physics, characteristic experiments were carried out using the advantages of RIXS. Charge excitation due to hole doped at oxygen sites in La_{2-x}Sr_xNiO_{4+δ}, La_{2-2x}Sr_{1+2x}Mn₃O₇, and La_{1-x}Sr_{1+x}MnO₄ was investigated in comparison with La_{2-x}Sr_xCuO₄ using elementary selectivity of O *K*-edge RIXS. Photon-in/photon-out process of RIXS enabled to probe electronic structure change due to metal-insulator transition in Ca₂RuO₄ induced by electronic field. Angle-resolved RIXS allowed us to measure the dispersion of elementary excitation in VO₂ and resonant inelastic X-ray diffraction from La_{1/3}Sr_{2/3}FeO₃. In electrochemistry of batteries, we have continuously studied mechanism of charge/discharge process and explored new electrode materials by ex-situ and operando RIXS. In order to clarify the effect of charge transfer between metal and oxygen, oxygen-free electrolyte battery cell is being developed. In 2018, several results for condensed matter physics were published, such as Fe *L*-edge RIXS of FeS

model complexes and low-spin ferrous and ferric iron complexes, V and Mn *L*-edge RIXS of half-metallic ferrimagnet Mn_2VAl , Cr *L*-edge RIXS of ruby, and Co *L*-edge RIXS of LaCoO_3 .

(4) Free-port station

The station is equipped with a focusing mirror chamber, and users can connect their own experimental chambers. In 2018, the following experiments were performed: time resolved soft X-ray diffraction of $\text{Ba}_3\text{CuSb}_2\text{O}_9$; time resolved X-ray absorption spectroscopy of Eu compounds with valence fluctuations; N *K*-edge near-edge X-ray absorption fine structure of 2D organic hetero-bilayer Cat-TTF/Im-SAM on Au; evaluation of spatial coherence of synchrotron radiation using coherent diffraction imaging technique; ambient-pressure X-ray photoemission spectroscopy of H_2 adsorption/absorption in Pd alloys and CO_2 hydrogenation reactions on Ni-based catalysts; element-selective analysis of 3D atomic structures of quasi-crystal $\text{BaTiO}_3(111)/\text{Pt}(111)$ thin film with photoelectron holography technique using Display type ELlipsoidal Mesh Analyzer (DELMA).