BL46XU
HAXPES II

1. Introduction

BL46XU is a beamline with an undulator light source. Until FY2021, two experimental apparatus, a multi-axis X-ray diffractometer and hard X-ray photoelectron spectroscopy (HAXPES), had shared operation. The multi-axis X-ray diffractometer was relocated to BL13XU at the end of FY2021, and BL46XU was reorganized as a beamline dedicated to HAXPES measurement techniques from FY2022 [1]. Therefore, the name of the beamline was changed to "HAXPES II". The upgrading of the beamline was carried out in the period between the end of FY2022 and the first half of FY 2023. In this upgrade, all optics equipment, except for a liquid-nitrogen-cooled double-crystal monochromator (DCM) with Si(111) reflection, were upgraded. The high-throughput HAXPES system was transferred to experimental hutch 1 (EH1) from experimental hutch 2 (EH2), and an ambient-pressure HAXPES system was installed into EH2. The details of these upgrades performed in BL46XU are as follows.

2. Beamline layout and optical components

The beamline layout is shown in Fig. 1. In the optics hutch (OH), a liquid-nitrogen-cooled DCM with Si(111) crystal pairs was installed. In this upgrade, two DCCMs were installed into the OH as high-resolution monochromators (HRMs) in order to achieve a narrower energy bandwidth of X-ray. The system of two DCCMs is equipped with two sets of channel cut monochromate crystals of Si(110) and Si(311). By switching them via horizontal translations, this system can change the energy resolution of the incident X-ray.

We evaluated the total energy resolution, which includes HAXPES analyzer resolution, for both Si(220) and Si(311) DCCMs in the incident X-ray energy range of 6.0–15 keV using the HAXPES system at EH1. The total energy resolution was estimated from measurements of Fermi-edge spectra of a gold sample at room temperature under the analyzer condition with a pass energy of 100 eV.

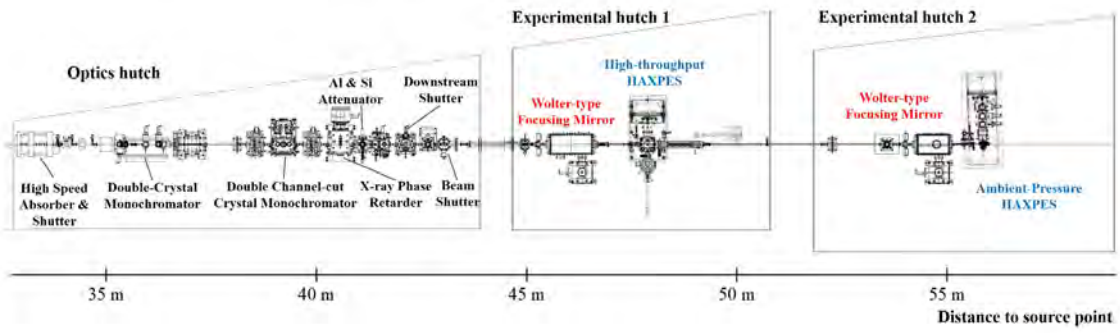

Fig. 1. Beamline layout of new BL46XU. All optical components, except for the focusing system, are located in OH. Two sets of photoelectron analyzers and focusing mirrors with different specifications are installed in EH1 and EH2.

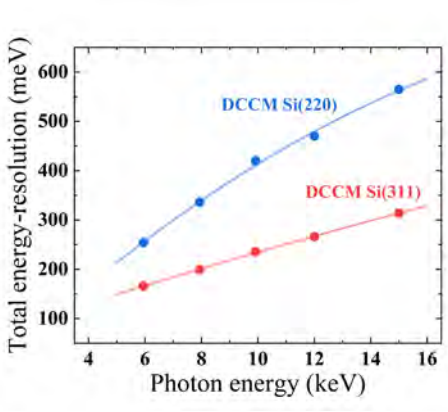

Fig. 2. Total energy resolution as a function of photon energy and the index of the DCCM crystal estimated from HAXPES measurements of the Fermi-edge spectra of a gold sample.

Figure 2 shows the total energy resolution for the Si(220)/(311) DCCMs as a function of the incident X-ray energy. Here, note that, for the data at the X-ray energies of 12 and 15 keV, the photoelectrons were measured by decelerating their kinetic energy to below 10 keV by applying positive bias to the sample [2]. With the Si(311) DCCM, photoelectron measurements with a high energy resolution ranging from 150 to 300 meV are achievable over the entire region. In contrast, the Si(220) DCCM has a relatively modest resolution although the X-ray flux is approximately four times higher than that with the Si(311) DCCM. Therefore, efficient measurements are possible by selecting an adequate DCCM for individual applications.

Monolithic Wolter-type mirrors were installed into EH1 and EH2 for the system that focuses the incident X-ray beam. The characteristics of these mirrors are their few adjustment axes and high tolerance to pitching error. These features simplify the procedure for adjusting the focus of the X-ray beam and make the beam conditions stable after focusing adjustment. Typical focused beam sizes are 2.0 μm (V) × 23 μm (H) and 1.0 μm (V) × 17 μm (H) for EH1 and EH2, respectively, when fully open with a primary slit in the front-end section (FE slit) located 28.9 m from the undulator source.

3. Upgrade of instrument control system

The system of controlling instruments was switched to the “BL774” system [3]. Recently, there has been an increasing need to perform advanced measurements by linking and controlling multiple instruments, such as automatic measurements with sample exchange. The BL774 system allows users to control devices with different specifications, such as motor-driven devices and piezo stages, in a unified manner without knowing the details of the instrument.

4. High-throughput HAXPES system

In EH1, we are developing a high-throughput automated HAXPES system for a number of samples in various research areas to alleviate the high competition of proposals for HAXPES in recent years. Figure 3 shows a photograph of the high-throughput HAXPES system. This system is based on the general-purpose HAXPES system previously installed at BL46XU EH2 and relocated to EH1, and a high-precision sample positioning mechanism (6-axis manipulator) and an automatic sample transfer mechanism have been installed. This system allows for the simultaneous introduction of a substantial number of samples into the vacuum, thereby enabling efficient sample transport and measurements. Also, we introduced the new analyzer control software "PEAK" launched by Scienta Omicron. PEAK is not limited

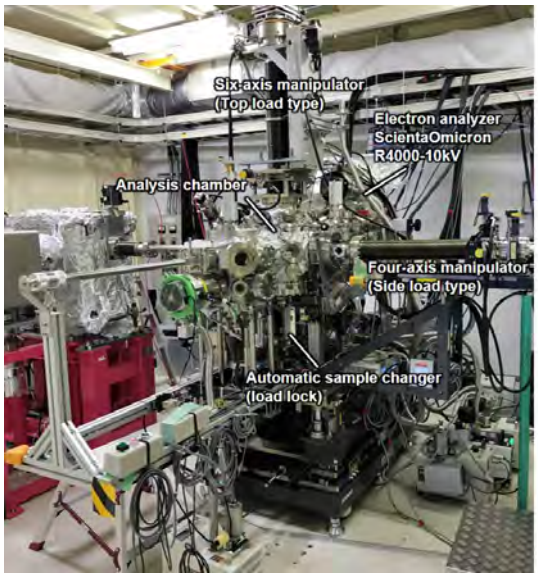

Fig. 3. Photograph of high-throughput HAXPES system in EH1.

to a web-based GUI, but also has a native Python-based external control API and is designed for the external control of the analyzer. In FY2024, we are developing an application for an automated HAXPES system fully operationally linked with PEAK software and BL774, which integrates measurement operation and control of equipment such as the auto–sample transfer, auto–position adjusting, and setting attenuator.

5. Ambient-pressure HAXPES system

An ambient-pressure HAXPES system was installed in EH2 (Fig. 4). This system enables the XPS measurements of samples in a gas atmosphere, which was not possible with conventional XPS systems that require high-vacuum conditions. The system maintains a vacuum in the analyzer, despite the increased gas pressure around the sample, through a small aperture in the front cone and a differential pumping stage located in front of the analyzer.

The HAXPES system, previously operated at BL36XU of SPring-8 since FY 2013, was relocated to BL46XU in FY 2023. A differential pumping-type electron energy analyzer (Scienta Omicron R4000 Hipp2) is employed. While the standard aperture diameter is 300 μm, allowing measurements up to 5000 Pa according to the manufacturer's specifications, a custom-made 30 μm aperture was utilized to extend the pressure range to atmospheric conditions.

By optimizing the aperture shape to match the focused beam profile of 1.0 μm (V) × 17 μm (H) at the new beamline, measurement efficiency was enhanced. A rectangular aperture 20 μm (V) × 80 μm (H) was fabricated as an alternative to the conventional circular aperture. This rectangular aperture yielded a threefold increase in signal intensity compared with the 30-μm-diameter aperture during vacuum measurements. Moreover, the analyzer pressure remained below 10^{-5} Pa even under atmospheric sample conditions.

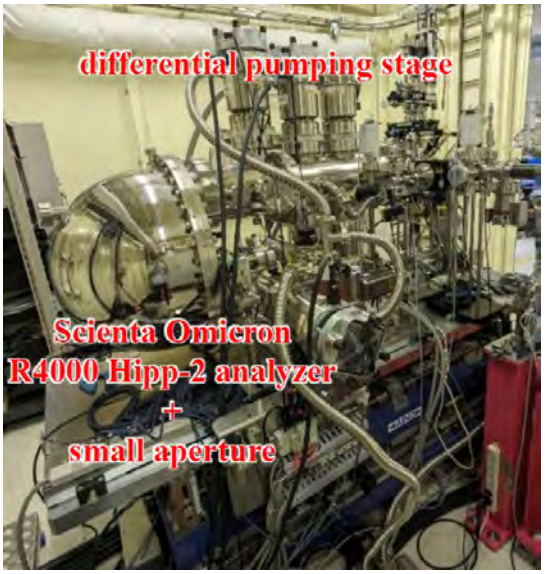

Fig. 4. Photograph of ambient-pressure HAXPES system in EH2.

Figure 5 shows the spectra of gases measured by introducing air at 10 kPa and water vapor at 4 kPa (saturated vapor pressure) into the measurement chamber. The incident photon energy was 7.94 keV. A survey scan of air reveals peaks attributed to atmospheric nitrogen and oxygen molecules. Notably, the O 1s peak from oxygen molecules in air exhibits 1.1 eV splitting due to the molecule's spin. In contrast, the O 1s peak from water molecules, 3.5 eV lower in binding energy than molecular oxygen, shows no splitting. These results demonstrate the capability of acquiring spectra reflecting the chemical state of oxygen atoms in gaseous environments.

The system's capability to operate in gas atmospheres enables the investigation of solid samples during gas–solid reactions. Future studies will focus on performing *in situ* measurements to monitor reaction processes. Additionally, the system will be utilized to analyze samples susceptible to desiccation by introducing them under water vapor conditions.

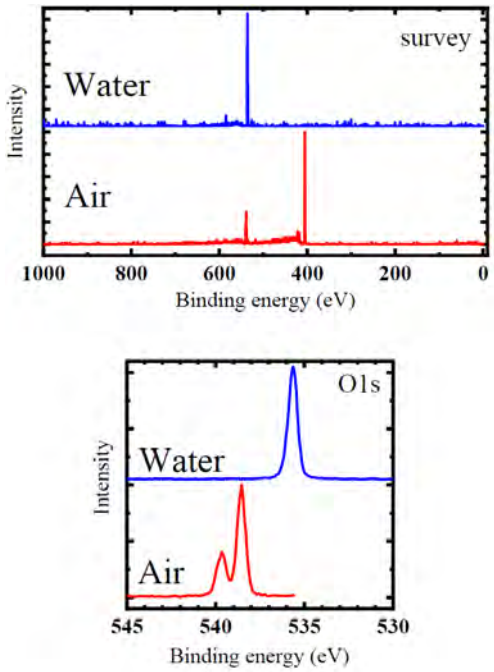

Fig. 5. HAXPES spectra at 10 kPa of air and 4 kPa of water vapor.

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References:

[1] Yasuno, S. et al. (2022). *SPring-8・SACLA Annual Report FY2022*, 92–95.

[2] Yasuno, S. et al. (2023). *Rev. Sci. Instrum.* **94**, 115113.

[3] Nakajima, K. et al. (2022). *J. Phys. Conf. Ser.* **2380**, 012101.