BL19B2
X-ray Diffraction and Scattering II

1. Introduction

BL19B2 is a bending magnet beamline dedicated to X-ray diffraction and scattering experiments. A versatile high-throughput powder diffractometer, and a multi-axis diffractometer are installed in the first hutch (EH1) and the second hutch (EH2), respectively. In the third hutch (EH3), a two-dimensional detector, PILATUS 2M, is installed for small-angle X-ray scattering (SAXS) experiments. The third hutch (EH3) offers camera lengths between 0.7 and 3 m, while EH2 provides a 41 m length known as ultrasmall-angle X-ray scattering (USAXS). In FY2023, the following developments were carried out in this beamline. The feasibility study on the application of grazing-incidence X-ray scattering (GIXS) to analyze the pair distribution function (PDF) of amorphous thin films was carried out using the multi-axis diffractometer in EH2. For the *in situ* SAXS/USAXS experiment, a system for controlling the humidity and temperature of the sample environment was developed. Furthermore, a new technique to ensure accurate information management in the measurement service was developed.

2. PDF Analysis of Amorphous Thin Films Using Grazing Incidence X-ray Scattering Techniques

We have investigated the feasibility of applying grazing-incidence X-ray scattering (GIXS) measurements with synchrotron radiation to the PDF analysis of amorphous thin films. The experiments for this feasibility study were carried out utilizing the versatile six-axis diffractometer installed at BL19B2 EH2. The samples for testing were amorphous tantalum oxide (a-TaO_x) thin films fabricated using pulsed laser deposition (PLD) on glass substrates under two different oxygen partial pressures: 5×10^{-5} Pa (Sample S1) and 1×10^{-2} Pa (Sample S2). The resulting TaO_x thin films had a uniform thickness of approximately 8.5 nm. In the experiments, the incident X-ray energy was precisely set to 12.398 keV using a Si(111) double-crystal monochromator in conjunction with a cylindrical mirror. The incident beam was carefully collimated to a height of approximately 0.2 mm and a width of 5 mm. A manual slit with an aperture of 0.03 mm was employed to create a narrow beam at the sample position, ensuring optimal beam conditions. The incident angle was accurately estimated using X-ray reflectivity (XRR)

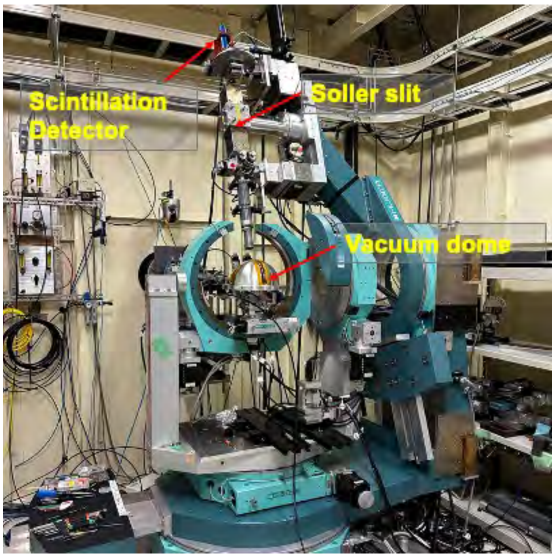

Fig. 1. Grazing-incidence X-ray scattering (GIXS) setup on the versatile multi-axis diffractometer installed at BL19B2 EH2.

measurements, which ensured that the X-ray beam was fully attenuated prior to reaching the glass substrate. The scattered X-rays from the sample were detected through a soller slit by the FMB $LaBr_3$ scintillation detector, which was scanned over a range of 1 to 141° in 0.1° increments in the vertical plane, covering a momentum transfer (Q) range of approximately 11.8 $Å^{-1}$. To minimize background signals resulting from air scattering, the film sample was mounted in a vacuum dome chamber attached to the sample stage, providing a controlled environment for the measurements.

The X-ray scattering data for the films meticulously corrected for background scattering, polarization effects, absorption, and Compton scattering are shown in Fig. 2(a). This figure shows clearly the difference between the scattering profiles of the samples, reflecting the difference in their amorphous structures. The corrected scattering intensities were then normalized by the atomic scattering factors to yield the total structure factor $S(Q)$, which encodes the structural information of the material [see Fig. 2(b)]. Furthermore, the PDF $g(r)$ was obtained by performing a Fourier transformation of $S(Q)$ and provides a detailed description of the atomic arrangement in real space. By utilizing advanced techniques such as PDF analysis and reverse Monte Carlo (RMC) simulations in combination with GIXS, researchers can gain deep insights into the three-dimensional atomic arrangement of amorphous materials. This approach unlocks valuable knowledge with far-reaching implications across a diverse array of scientific and technological endeavors.

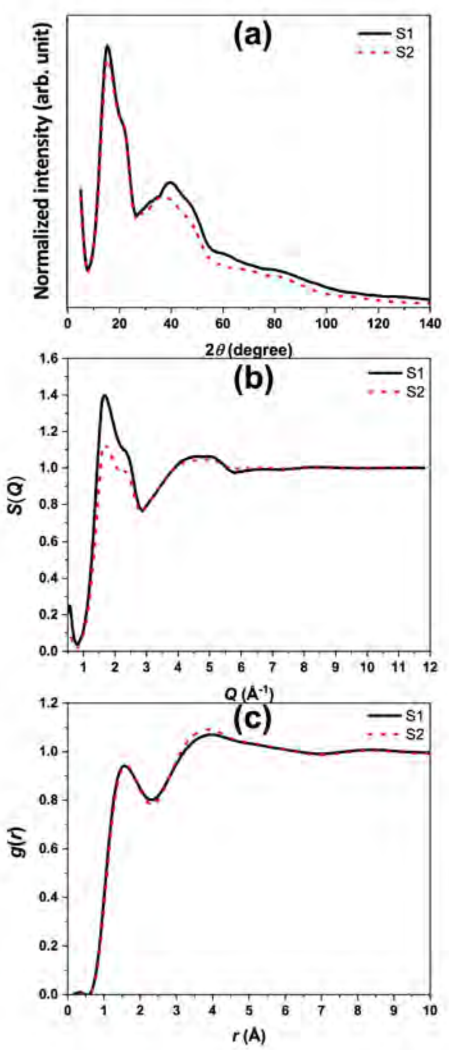

Fig. 2. (a) GIXS patterns, (b) total structure factor, $S(Q)$, and (c) pair distribution function $g(r)$ of TaO_x thin films with 5×10^{-5} Pa (S1) and 1×10^{-2} Pa (S2) oxygen partial pressures.

3. Development of Apparatus for Controlling Humidity and Temperature of Sample

Environments in SAXS/USAXS Experiments

We developed a system that allows the precise regulation of the humidity and temperature of sample environments in *in situ* SAXS/USAXS measurements. The system consists of a sample chamber combined with a temperature controller (HCS302, INSTEC) and a humidity generator

(HUM-1, Rigaku).

Figure 3(a) shows the humidity-conditioning sample chamber attached to the temperature controller while Fig. 3(b) illustrates the sample mount for the sample chamber. The sample mount can be inserted from the side of the sample chamber. This layout facilitates sample exchange and enhances the efficiency of *in situ* SAXS/USAXS measurements with controlled humidity. We have confirmed that the system currently achieves temperature and humidity control up to 70 °C and 85% RH without condensation forming inside the chamber. This device enables the study of materials under conditions that mimic those in various applications, including fuel cell membranes, plant fragments such as wood, and biomimetic materials.

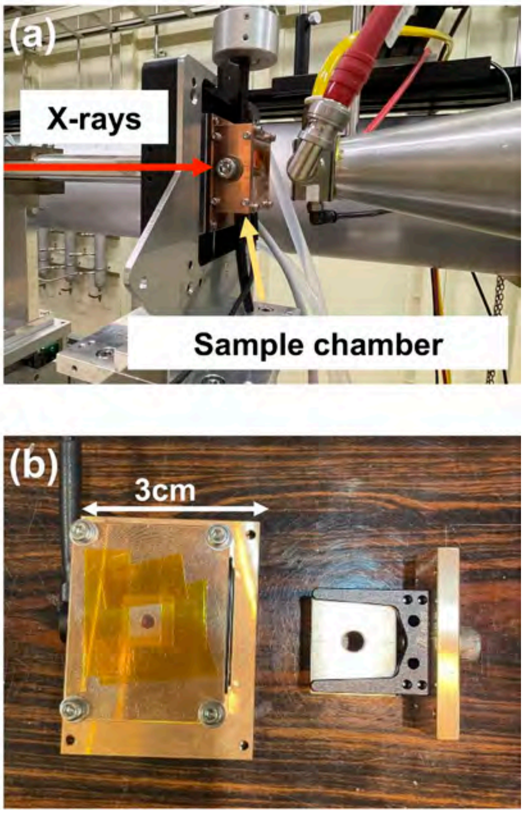

Fig. 3. (a) Humidity-conditioning sample chamber and (b) sample mount.

To address the demand for material performance evaluation under high temperature and humidity conditions—which is particularly relevant in fields such as fuel cell membrane development and wood processing—the chamber will undergo further improvements in the future.

4. Sample Information Management Using NFC

In BL19B2, a measurement service [1] utilizing automated measurement systems for powder diffraction [2] and SAXS/USAXS [3] measurements is provided. This service offers the convenience of allowing users to mail their samples. On the other hand, there is a risk that the instrument operators may mistake the samples and measurement conditions or damage them during handling. To prevent such risks and ensure accurate information management, we developed a new technique using near-field communication (NFC) tags.

We developed dedicated software for reading and writing data on NFC tags, as shown in Fig. 4. Sample information is managed for each sample holder package for storing and transporting samples between users and SPring-8. A one-time passcode randomly generated by our software is recorded on an NFC tag attached to the package. Users upload sample contents and measurement conditions to a dedicated data server using the passcode, which acts as a key to link the package with information such as the proposal number, project leader, and measurement conditions. This allows operators to perform measurements without the need to handle the samples or confirm the link between the samples and the measurement conditions.

Fig. 4. Dedicated software for reading and writing data on NFC tags.

OSAKA Keiichi, KUMARA Rosantha, and ITO Kanae

Industrial Application and Partnership Division, JASRI

References:

[1] https://user.spring8.or.jp/?p=42152

[2] Osaka, K. et al. (2019). *AIP Conference Proceedings* **2054**, 050008.

[3] Osaka, K. et al. (2016). *AIP Conference Proceedings* **1741**, 030003.