

## 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, *Polaris* <sup>[1]</sup>, 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 0.7–3 m, while the EH2 provides a 41-m length known as USAXS, ultrasmall-angle X-ray scattering. In FY2022, the following developments of experimental techniques were carried out in this beamline. In EH1, *Polaris* equipped with multi-soller slits was investigated for application to the high-throughput measurement of XRD on thin-film samples. In EH2, the measurement technique of the diffraction anomalous fine structure (DAFS) was studied using the multi-axis diffractometer. For *in situ* SAXS/USAXS measurements of reactions of liquid samples, an apparatus that automatically adds reaction liquid agents to the liquid sample by dripping and stirring was developed.

#### 2. Application of a versatile high-throughput powder diffractometer, *Polaris*, equipped with multi-soller slits to XRD measurement on thin-film samples

The versatile high-throughput powder diffractometer, *Polaris*, installed in the EH1, is equipped with a multi-soller slit system so that it can be applied to the XRD measurement of

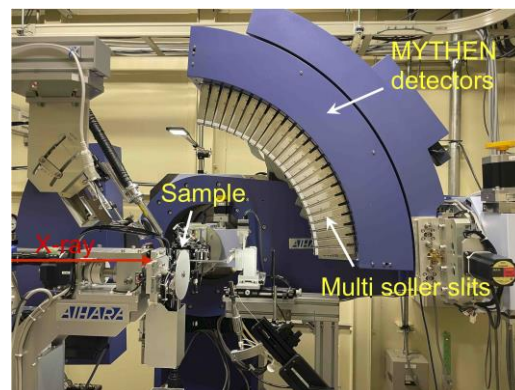


Fig. 1. High-throughput *Polaris* diffractometer installed in EH1 combined with multi-soller slit system and MYTHEN detectors.

plate-shaped samples such as thin-film samples under reflection geometry. In Fig. 1, *Polaris* equipped with the multi-soller slit system is shown. The multi-soller slit system consists of 24 soller slits and is mounted between samples and the one-dimensional MYTHEN detectors. Each soller slit of the system can restrict the direction of detecting X-rays scattered from the samples by detectors, and therefore functions as a pseudo-zero-dimensional detector. These soller slits are located so that the diffraction angles,  $2\theta$ , of the detected diffracted X-ray are every  $3.4^\circ$ . Therefore, diffraction profiles in a wide range of  $2\theta$  can be obtained by scanning the  $2\theta$  axis of the diffractometer over a range of  $\pm 3^\circ$  and merging the profiles detected by each soller slit.

In Fig. 2, diffraction profiles of Zn-doped  $\text{Cu}_2\text{O}$  polycrystalline thin films ( $\text{Zn}:\text{Cu}_2\text{O}$ ) measured using the multi-soller slit system (indicated by red line) are shown along with those

measured without soller slits (indicated by blue line). The incident angle of the X-ray to the sample surface was  $0.5^\circ$ . As shown in Fig. 2(b), the peak profile measured without the multi-soller slit system (blue line) was directly influenced by the shape and intensity distribution of the footprint of the X-ray irradiated on the sample surface, and resulted in splitting and broadening. However, that measured with the multi-soller slit system (red line) was sharp because of the effect of the scattering angle resolution of soller slits.

The Debye–Scherrer camera layout of *Polaris* is useful for the high-throughput measurement of XRD data with a wide range of diffraction angles. However, because transmission

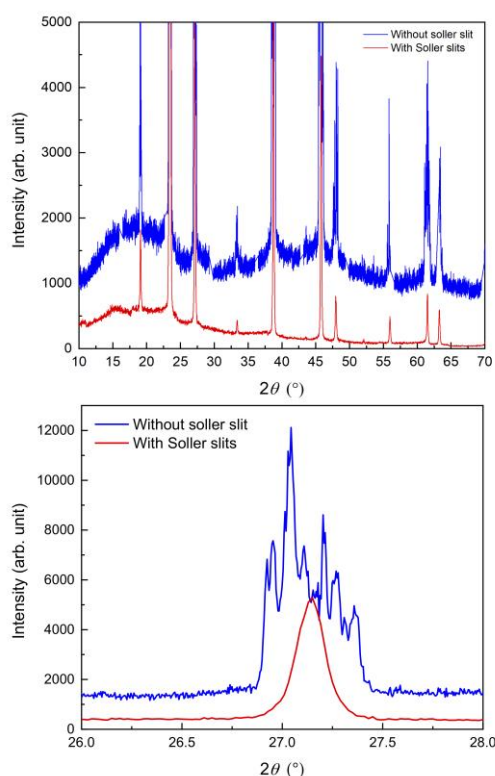


Fig. 2. Diffraction profiles of Zn:Cu<sub>2</sub>O thin films measured with and without soller slits. (a) Profile in a wide range of  $2\theta$ , and (b) peak profile at  $2\theta=27^\circ$ .

geometry is required for sample setting, it is not suitable for measurement on samples with large absorption of X-rays. Therefore, this slit system is considered to be useful for anomalous X-ray diffraction (AXRD) measurements of samples containing  $3d$  transition metals with absorption edges of low energy, such as Fe, Co, Ni, Cu, and Zn.

### 3. Experimental technique of diffraction anomalous fine structure measurement

The multi-axis diffractometer installed in EH2 is used in various research fields. Recently, in the field of semiconductor materials, there has been a demand to characterize the chemical state or local structure of elements in each layer of multilayer thin films composed of multiple materials whose compositions include the same kind of elements, such as Si<sub>x</sub>Ge<sub>1-x</sub> thin film formed on a Ge substrate. X-ray absorption fine structure (XAFS) is a well-established method to investigate both the chemical state and local structure of targeted elements in materials. However, XAFS measurement provides information averaged over the entire sample, so it may be difficult to identify the materials composing the multilayer thin films. The diffraction anomalous fine structure (DAFS) measurement utilizes the anomalous effect around absorption edges on the X-ray diffraction from materials. Therefore, this technique can be used to investigate the chemical state and local structure of targeted elements to identify the materials composing the multilayer thin films. In FY2022, we study the measurement of DAFS using the multi-axis diffractometer.

Figure 3 shows (a) a schematic illustration and (b) a photograph of the DAFS measurement setup. The DAFS spectrum can be obtained by detecting the diffraction intensity as a function of the incident X-ray energy around the absorption edge. The incident X-ray energy was tuned by a double-crystal monochromator. The diffracted X-rays from the sample were detected by a  $\text{LaBr}_3:\text{Ce}^{3+}$  scintillation detector (FMB Oxford). A pair of receiving slits [S2 and S3 shown in Fig. 3(a)] was set between the sample and the scintillation detector to minimize background signals. A seven-element silicon drift detector [7-SDD shown in Fig. 3(a)] was also installed to perform fluorescence XAFS measurements simultaneously with DAFS measurements.  $\text{Si}_x\text{Ge}_{1-x}$  thin film formed on a Ge substrate was chosen as the sample in this measurement.

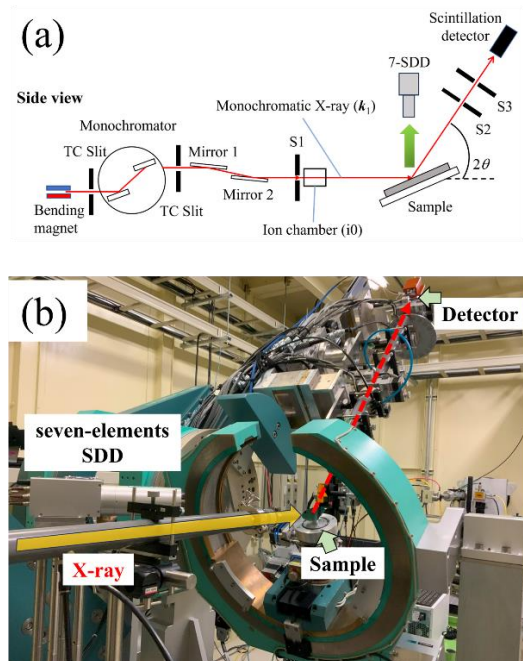


Fig. 3. Developed DAFS measurement setup.  
(a) Schematic illustration. (b) Photograph.

Firstly, we confirmed the diffraction pattern of the sample. Figure 4(a) shows the 004 diffraction of the  $\text{Si}_x\text{Ge}_{1-x}$  thin film and Ge substrate. The X-ray energy was 11.250 keV in this measurement. The diffraction peaks originating from the Ge substrate and  $\text{Si}_x\text{Ge}_{1-x}$  thin film were successfully observed at  $2\theta = 45.856^\circ$  and  $46.684^\circ$ , respectively. Secondly, we measured the integrated intensity of  $\text{Si}_x\text{Ge}_{1-x}$  thin films as a function of incident X-ray energy around the Ge-K absorption edge. Figure 4(b) shows the DAFS spectrum from  $\text{Si}_x\text{Ge}_{1-x}$  thin films. The DAFS spectrum of the sample was collected using 004 diffraction peaks at 453 points of energy from 10.774 to 11.851 keV. A continuous spectrum was successfully obtained by dividing the integrated intensity of the 004 diffraction peak by the incident X-ray intensity measured in an ionization chamber [i0 shown in

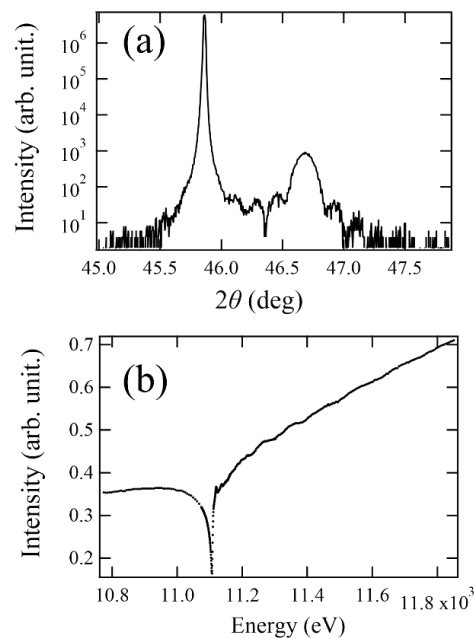


Fig. 4. (a) 004 diffraction of  $\text{Si}_x\text{Ge}_{1-x}$  thin film and Ge substrate. (b) DAFS spectrum from  $\text{Si}_x\text{Ge}_{1-x}$  thin film.

Fig. 3(a)]. As a result of this development, we could observe a clear DAFS spectrum.

#### 4. Development of an automated reaction liquid agent apparatus for *in situ* SAXS/USAXS measurement on reactions of liquid samples

We have developed an apparatus that automatically adds reaction liquid agents to liquid samples by dripping and stirring for *in situ* SAXS/USAXS measurements of reactions of liquid samples. The overview of this apparatus is shown in Fig. 5. The liquid sample was filled in a plastic cell with a square rod shape of a 10-mm-square cross section set on a small magnetic stirrer stage. The temperature of the sample can be controlled at around room temperature by using a heater. To drip the reaction liquid agent into the liquid sample, this system utilizes the syringe infusion pump (FP-1100W, made by MELQUEST). Because the stirrer stage and the syringe infusion pump can be controlled remotely, it is possible to adjust the timing for dripping the reaction agents and stirring the sample with reaction agents to match time-resolved *in situ* measurements of reactions of liquid samples. We applied this apparatus in a user experiment in which the rennet-induced

coagulation reaction of milk for cheese production was observed by time-resolved *in situ* USAXS measurement.

Osaka Keiichi, Kumara Rosantha, Watanabe Takeshi, and Ito Kanae

Industrial Application and Partnership Division,  
JASRI

#### Reference:

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

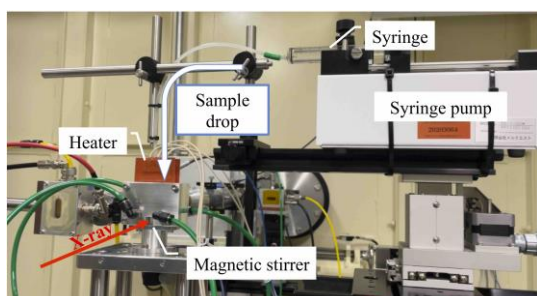


Fig. 5. Sample drop with the syringe pump.