Sumitomo Electric Beamlines for Materials Characterization Using Synchrotron Radiation

Koji YAMAGUCHI*, Junji IIHARA, Shigeaki UEMURA, and Yoshihiro SAITO

Using strong synchrotron x-rays, advanced characterization can be performed for chemical-bonding states, atomic structures, and chemical reactions. We have constructed beamlines of our own called "Sumitomo Electric Beamline" in the SAGA Light Source to develop new materials and devices as well as improve existing products with advanced characterization. In our two beamlines using hard and soft x-ray, absorption spectroscopy, diffraction measurement, small-angle scattering, and photoelectron spectroscopy are performed. We began the construction of the beamlines in February 2015 and started operation in November 2016.

Keywords: synchrotron radiation, x-ray absorption spectroscopy, diffraction, small-angle scattering, photoelectron spectroscopy

1. Introduction

The extremely high intensity x-ray from synchrotron radiation*1 is very useful for precisely analyzing the chemical bonding states and atomic structures of materials as well as chemical reactions in production processes. Sumitomo Electric Industries, Ltd. has used synchrotron radiation analysis in development of materials, devices, and production processes, as well as in investigation of failure mechanisms of products.[1]-[4] Despite the growing need for the synchrotron radiation analyses, it was difficult to secure beam time as long as depending on the beamlines in public synchrotron radiation facilities.

To solve the above problem with time restrictions, we commenced a study in 2011 toward the installation of beamlines that can preferentially be used by Sumitomo Electric and its group companies. We started the construction of these beamlines, called "Sumitomo Electric Beamline," in 2015 at the Kyushu Synchrotron Light Research Center (SAGA Light Source)*2 established by Saga prefecture.[5] Since the start of operation in November 2016, the Beamline has been used for various analyses.

This paper details the constituent equipment of the Beamline and the analyses that can be conducted by this facility.

2. Constituent Equipment of Beamline

The Sumitomo Electric Beamline was designed to enable the use of x-rays with a wide energy range from 0.05 keV to 35 keV, which is necessary to analyze a various kinds of constituent elements in our products. This is particularly important in the analysis by the x-ray absorption spectroscopy technique, in which the energy of x-ray is tuned near the absorption edge of the elements, as described later in detail.

In order to cover the wide energy range of x-ray, two beamlines were installed. One is a hard x-ray beamline (BL16), which covers an energy range of 2 keV to 35 keV, while the other is a soft x-ray beamline (BL17), which covers an energy range of 0.05 keV to 2 keV. The overall plan view and specifications of the Beamline are given in Fig. 1 and Table 1, respectively.

The x-ray source, transport channel, and measurement instrument are described in the following sections.

3. X-ray Source and Transport Channel

An x-ray from a synchrotron radiation source is a mixture of x-rays of various energies, and is divergent. The

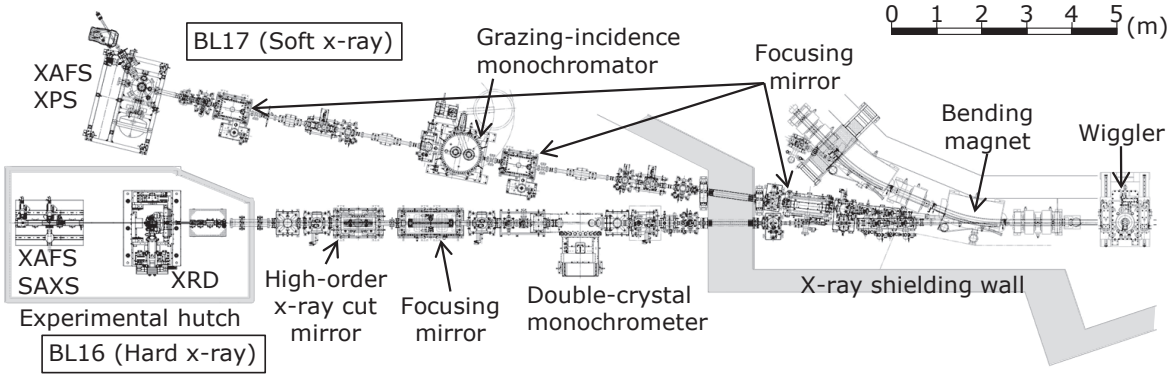

Fig. 1. Constituent equipment of Beamline

Table 1. Specifications of beamline

	Hard x-ray beamline: BL16	Soft x-ray beamline: BL17
X-ray source	4T superconducting wiggler	Bending magnet
Monochrometer	Double-crystal monochrometer InSb111, Si111, Si311	Grazing-incidence monochromator 400/1000/1400/2200 lines/mm
Photon energy	2 keV – 35 keV	0.05 keV – 2 keV
Photon flux	10^{10} photons/s @ 10 keV	10^{9} photons/s @ 0.6 keV
Energy resolution	E/ΔE = 5000 @10 keV	E/ΔE = 3600 @0.4 keV
Spot size	1 mm (horizontal) × 0.2 mm (vertical)	1 mm (horizontal) × 0.05 mm (vertical)
Measuring technique	X-ray absorption spectroscopy, x-ray diffraction, Small-angle x-ray scattering	X-ray absorption spectroscopy, x-ray photoelectron spectroscopy

transport channel tunes the x-ray having the energy suitable for a specific measurement, and focuses the x-ray on the measuring sample with sufficient intensity. Each beamline is described in the following sections.

3-1 Hard x-ray beamline: BL16

The x-ray source of the hard x-ray beamline (BL16) is a 4T superconducting electromagnet wiggler,*3 which is located in the straight portion of the electron storage ring.(6)

A double-crystal monochrometer has been installed in the beamline to tune the x-ray having the energy optimal for a specific measurement among the x-rays emitted from the wiggler.

Three types of crystals (InSb111, Si111, and Si311) have been prepared to enable the use of an x-ray within a wide energy range of 2 keV to 35 keV by selectively using one of them.

The cylindrical mirror is used to focus the divergent x-ray from the source onto the measuring sample. The plane mirror removes unusable high-order x-rays.

Figure 2 shows the intensity of the x-rays (photon flux) that can be used for practical measurements. This intensity was measured at the sample position in the experimental hutch of BL16. It is indicated in terms of the photon flux that was converted from the current obtained in the ion chamber located in the experimental hutch.

As described above, it was confirmed that BL16 can generate x-rays of up to 35 keV with sufficient intensity, and the energy resolution E/ΔE is 5000 at 10 keV.

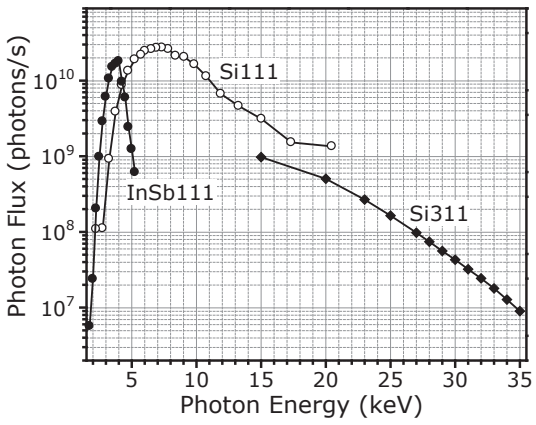

Fig. 2. X-ray intensity (photon flux) of BL16

3-2 Soft x-ray beamline: BL17

A 1.46T bending electromagnet*4 in the electron storage ring is used as the x-ray source of BL17.(5) As for the transport channel, three focusing mirrors and a grazing-incidence monochrometer with varied-line-spacing plane grating are installed.(7)

Four diffraction gratings with 400, 1000, 1400, and 2200 lines/mm are selectively used depending on the energy to be used and required energy resolution.

Soft x-rays are easy to be absorbed even when they pass through a tenuous gas. To prevent the deterioration of the intensity, the entire beam path is maintained at ultra-high vacuum.

The intensity of x-rays (photon flux) at the sample position is shown in Fig. 3. This intensity was determined from the current produced by a photodiode placed in the ultrahigh vacuum chamber. The energy resolution E/ΔE, which was determined from the nitrogen gas transmission spectrum, was 3600.

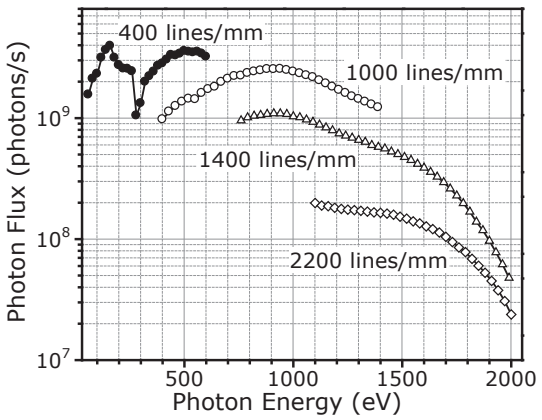

Fig. 3. X-ray intensity (photon flux) of BL17

4. Measurement Techniques and Measuring Instruments

An outline of each measurement technique and measuring instrument used in each beamline, as well as the results of trial measurements, are described below.

4-1 Hard x-ray absorption spectroscopy (XAFS)

XAFS is a technique for acquiring the information on

the chemical state and coordination of an element from the x-ray absorption spectrum. In practice, the x-ray absorbance of the sample is measured by scanning energy of incident x-ray near the absorption edge of the element. For transmission XAFS measurements, two ionization chamber and measurement system are installed to measure intensities of incident and transmitted x-rays precisely.

For bulk samples and other materials through which x-rays cannot pass, a four-element silicon drift detector (SDD) is installed to measure fluorescent x-rays from the sample. We also install converted electron detector that measures secondary electrons emitted from the sample. These devices are used for fluorescence XAFS measurements and electron yield XAFS measurements.

To analyze the surface of sample, a sample stage is installed that can control x-ray incident angle precisely with respect to the sample. Depending on the objective of the measurement and properties of the sample to be measured, these measuring instruments and sample stage can be relocated as needed on the optical table installed on the downstream side inside the experimental hutch.

Further, the beamline includes a chamber located on the optical table upstream side of the experimental hutch. This chamber, which is filled with helium gas to avoid attenuation of incident x-ray, enables us to measure fluorescence and electron yield XAFS of sulfur, phosphor, and other elements with low absorption edge energy.

Figures 4 and 5 show examples of XAFS spectra measured in BL16. The XAFS spectrum shown in Fig. 4 was measured for phosphor under a helium gas atmosphere. The absorption edge energy of phosphor is nearly equal to the lower limit of the energy that can be used in BL16. In contrast, Fig. 5 shows the XAFS spectrum of tin, whose absorption edge energy is close to the upper limit of the energy used in BL16. Both of the spectra shown in the above figures are distinct enough to define the difference between the shapes of different chemical compounds.

4-2 X-ray diffraction (XRD)

XRD is a technique for determining the crystal structures, distortions, or residual stress in crystalline materials. In practice, a monochromated x-ray beam is irradiated to a sample and the direction (diffraction angle) and intensity of the diffracted x-ray are measured precisely. The diffractometer used in the beamline has nearly the same function as commercially available equipment. However, the sample stage capable of holding a sample measuring up to 100 mm × 100 mm × 100 mm in size and 10 kg in weight makes it possible to measure even large-sized parts and control the measurement atmosphere, thereby expanding the range of measurable samples. A diffractometer of this size can provide precisely parallel incident x-rays and is therefore particularly useful for precision measurement by synchrotron radiation.

Figure 6 shows the diffraction pattern obtained from an approximately 10 nm thick gold film formed on an Si wafer. This figure verifies that BL16 can be used for measuring sufficiently precise diffraction intensity of a very thin film.

4-3 Small-angle x-ray scattering (SAXS)

SAXS is a technique for quantifying the microstructures of resin and other materials. This technique can quantify the sizes and dispersion of structures from the intensity distribution of x-rays that are scattered at angles smaller than the x-ray diffraction.

In BL16, a two-dimensional detector is placed on the optical table located on the downstream side in the experimental hutch, while the sample is placed on the optical table located on the upstream side. A depressurized pipe has been located between the detector and sample to prevent x-rays from being scattered by ambient air. We can take a picture

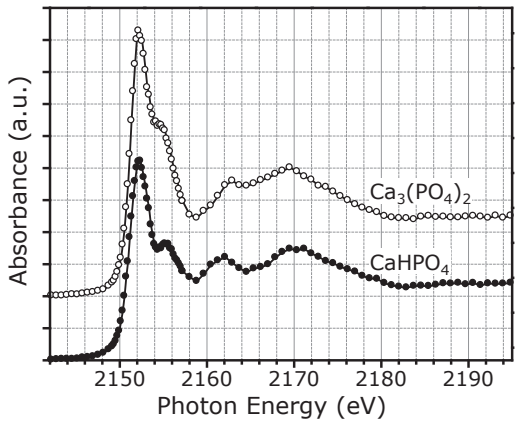

Fig. 4. Electron yield XAFS spectrum of phosphor

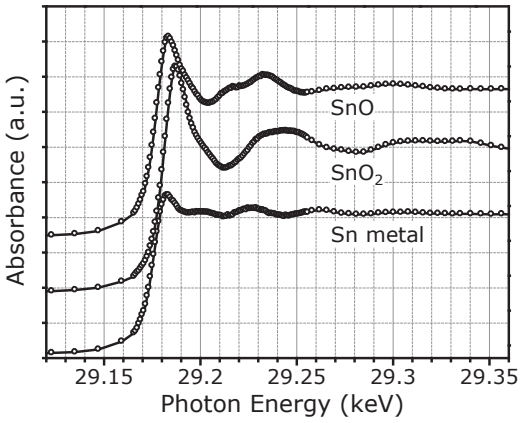

Fig. 5. Transmission XAFS spectrum of tin

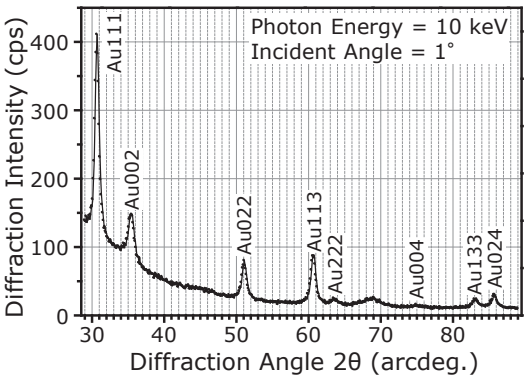

Fig. 6. X-ray diffraction pattern of gold thin film

with the size of approximately 200 mm^2 by scanning the detector in both vertical and horizontal directions.

In the above standard device layout, the distance between the sample and detector (camera length) is 3 m. However, the camera length can be adjusted in a range of 0.3 m to 3 m by setting the sample on the diffractometer or the optical table located on the downstream side of the experimental hutch.

Figure 7 shows the SAXS measurement result for silver behenate that is used as the standard sample for small-angle x-ray scattering. This figure verifies that a scattering profile can be obtained from a two-dimensional scattering pattern.

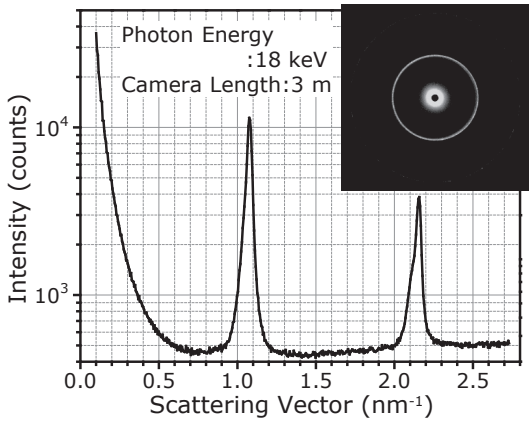

Fig. 7. Small-angle x-ray scattering profile of silver behenate and scattering pattern (upper right)

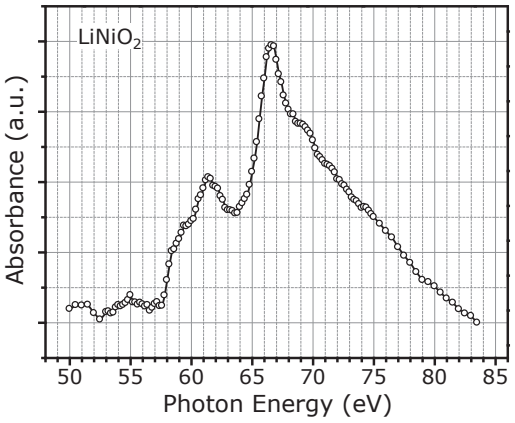

Fig. 8. Electron yield XAFS spectrum of Li contained in $LiNiO_2$

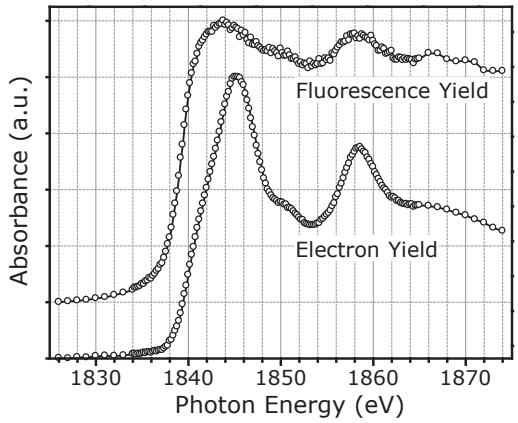

Fig. 9. Fluorescence yield and electron yield XAFS spectra of Si contained in SiC

4-4 Soft x-ray absorption spectroscopy (XAFS)

As a soft x-ray usually cannot pass through samples, BL17 is equipped with measuring instruments installed in an ultrahigh-vacuum chamber to measure the fluorescence x-ray emitted from the sample and/or the current flowing through the sample to perform XAFS measurements.

Figure 8 shows XAFS the spectrum of lithium in $LiNiO_2$. It is impossible in principle to measure hydrogen and helium by XAFS. It has been confirmed that BL17 can measure the lightest element among those for which XAFS can be used.

Figure 9 shows the XAFS spectra of silicon, whose absorption edge is close to the upper limit of the energy range of BL17. The difference in spectrum profile between the electron yield and fluorescence yield reflects the dependence of the chemical bonding state on measurement depth.

4-5 X-ray photoelectron spectroscopy (XPS)

XPS is a technique for acquiring information on the composition and chemical state of the sample surface using the energy distribution of photoelectrons emitted from the sample surface when it is irradiated with an x-ray. While a wide variety of equipment is commercially available, the strongest advantage of XPS using synchrotron radiation is that it can control the escape depth of photoelectrons by controlling the energy of incident x-rays. This enables us to analyze top surfaces of the sample, which is impossible with commercial equipment.

Figure 10 shows an XPS spectrum of silicon wafer with incident x-ray energy of 700 eV. This figure clearly shows the presence of a native oxide layer at the top surface of an as-received wafer. In addition, the split of Si2p peaks prove that the measurements with very high

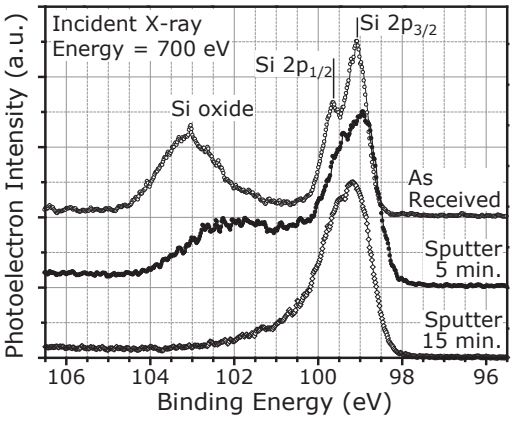

Fig. 10. XPS spectrum of Si wafer surface

energy resolution can be performed. This figure also shows that the oxide layer on the surface starts to disappear when this wafer is subjected to ion sputtering in the measurement chamber.

5. Conclusion

This paper has outlined the Sumitomo Electric Beamline we installed at the SAGA Light Source. We can use it for synchrotron analysis on a priority basis. For one year after the start of operation, we have used this facility to analyze a variety of materials and devices. We will continue to enhance the performance and efficiency of the facility to expand its use for the solution of various challenges and thereby accelerate the development of new products and upgrade the quality of our existing products.

6. Acknowledgments

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Technical Terms

∗1 Synchrotron radiation: When the path of an electron traveling at close to the speed of light is bent, an extremely strong white electromagnetic wave is produced in a direction tangent to the path. This electromagnetic wave is called synchrotron radiation.

∗2 Kyushu Synchrotron Light Research Center: A synchrotron radiation facility with stored electron energy of 1.4 GeV, which was established in Tosu city by the Saga prefectural government. Saga Prefectural Regional Industry Support Center runs and manages the facility. Its shared use started in February 2006.

∗3 Wiggler: The upper limit of x-ray energy that can be used for synchrotron radiation spectroscopy depends on the energy of electrons and the curvature of their path. To obtain a high-energy x-ray, it is necessary to increase the electron energy or reduce the curvature of the electron path. Since the electron energy is fixed for each synchrotron radiation facility, reducing the curvature of the electron path is the only alternative for a specific facility to obtain a high energy x-ray. In practice, a device comprised of a superconducting electromagnet that produces a powerful magnetic field is located in the electron path. This device is called a wiggler.

∗4 Bending electromagnet: An electromagnet for bending an electron path to revolve the electrons along the storage ring. When the electron path is curved, synchrotron radiation is produced in a direction tangent to the path.

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