BL17SU
RIKEN Coherent Soft X-ray Spectroscopy

1. Introduction

As we have noted in the previous SPring-8/SACLA Annual Report FY2020, BL17SU has been operated as a beamline dedicated mainly to spectromicroscopic studies in the last few years. Nowadays, more than 70% of the total user time of BL17SU, including public use, is devoted to spectromicroscopic experiments. While utilizing two spectromicroscopes, *i.e.*, the versatile PEEM [1] and the scanning soft X-ray (SX) microscope [2], as the main equipment, we have been operating the beamline together with advancing the launch of a new scanning SX microscope with high spatial resolution and counting efficiency, and also the sophistication, including the development of an automatic measurement system, for the angle-resolved photoelectron spectroscopy (ARPES) apparatus.

At the end of 2020, it was unfortunate that water leakage was found in the coil of the electromagnet used in the novel insertion device, ID17, called the multi-polarization-mode undulator [3]. After a few weeks of the shutdown, it was decided to operate ID17 as the vertical undulator using permanent magnets only, without using electromagnets. Since then, the operation of BL17SU resumed under the constraints of non-polarization switching capability, the reduction in energy range as well as the reduction in photon flux.

At the beginning of 2021, it was decided to build a new insertion device specific to the SX energy region, called a Helical-8 undulator [4], to overcome these constraints. Design work was initiated in early 2021 and the construction of the new ID17 began at the beginning of FY2021. The new ID17 will be installed during the summer storage-ring shutdown period in FY2022.

2. Recent activities

2.1 Development of high-spatial-resolution scanning SX spectromicroscope

In FY2021, we mainly advanced research and development on a new scanning SX spectromicroscope. It is a sub-100-nm-resolution spectromicroscope with an order of magnitude higher spatial resolution than the existing submicron-resolution spectromicroscope [2]. Both hardware and application software are designed to be based on the concept of modular architecture. Optical elements for focusing the SX beam, such as a Fresnel zone plate (FZP) and an order sorting aperture (OSA), are mounted on the XYZ submicron-resolution feedback-stage module, and the sample to be observed is mounted on the 1-nm-resolution feedback-stage module so that more accurate control can be realized. Only a center beam stop (CBS) is controlled by an XZ submicron-resolution feedback-stage module. These four feedback-stage modules can be freely reconfigured on a 445 mm × 750 mm baseplate. The feedback-stage modules are mounted on this baseplate, which can be taken out from the vacuum chamber. On the baseplate, all the feedback-state modules are precisely aligned using an alignment laser and then returned to the vacuum chamber along with the baseplate. After that, further precise alignment is performed using synchrotron radiation to obtain an SX probe for achieving a sub-100 nm resolution.

Spectromicroscopic experiments using this apparatus can be carried out in two different modes. One is based on a transmission arrangement, a mode that uses the so-called scanning transmission X-ray microscopy (STXM), in which a sub-100 nm SX probe transmitting an ultrathin sample is detected by a photodiode or a CCD sensor located downstream of the sample and the absorbance of the sample is measured. Another mode is to measure fluorescent X-rays emitted from the sample surface with a multi-element silicon drift detector (SDD) system in a reflective arrangement enabling the observation of a thick sample. The number of SDDs is currently two, but it is designed to be expanded to eight in the future.

Figure 1(a) shows a photograph of an exterior view of a new SX spectromicroscope. The apparatus is housed in a light-shielding booth (with fluorescent lights inside) so that the ceiling light of the experiment hall can be shielded. Figure 1(b) shows a picture indicating the components around the sample area. In addition to FZP, OSA, and the sample stage (SS), the current two SDD elements are shown. Figure 1(c) represents a transmitted image of a calibration standard sample (manufactured by Applied Nanotools) for evaluating the focusing performance of the microscope. The SX energy was 1860 eV, and it was designed to achieve a focus of about 90 nm in this energy range. When Fig. 1(c) was observed, the optics were adjusted to the status where the 100 nm line & space could be recognized. When the energy of the SX probe was tuned to be 600 eV, it was designed to achieve a resolution of about 30 nm. At

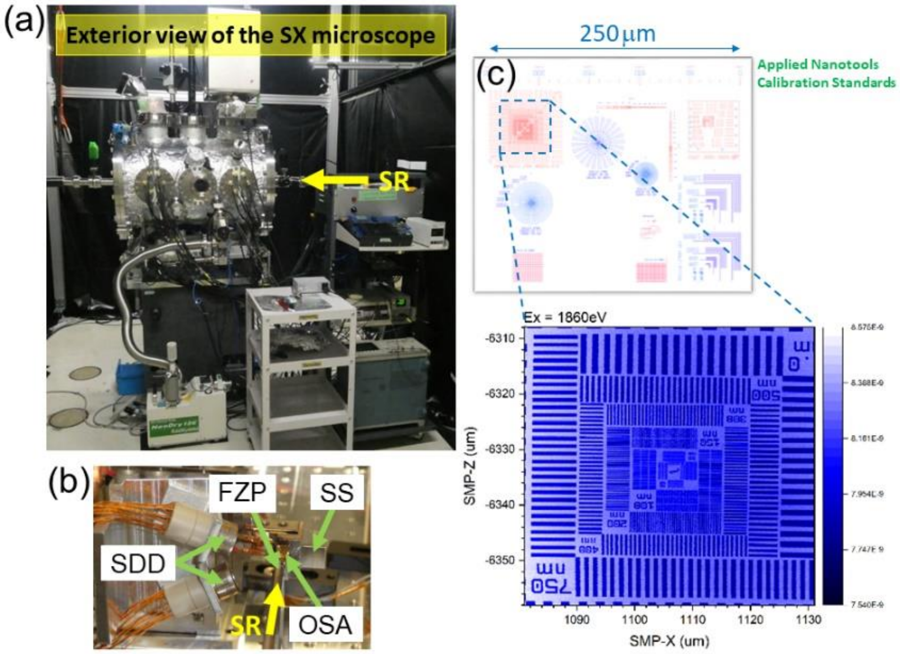

Fig. 1. (a) Photograph of the high-spatial-resolution scanning SX spectromicroscope. (b) Picture around the sample area of the new spectromicroscope. (c) Entire image of the test pattern for the calibration of the focusing optics (upper) and the intensity mapping of the transmitted 1860 eV SX probe.

present, it has been confirmed that the SX beam can be focused to a level where the 25 nm line & space can be recognized. In the future, it will be further adjusted to work as a microscope with a sub-100 nm spatial resolution in all the energy ranges and to increase the counting efficiency by increasing the number of SDDs.

After the spectromicroscopic experiment, all the optical components and samples are removed from the SX beam axis so that synchrotron radiation can be directed to the experimental apparatus installed downstream.

2.2 Study of adhesive interface using a submicron-resolution SX spectromicroscope

Research and development using an existing submicron-spatial-resolution spectromicroscope [2] is being diligently continued, and also the apparatus is being considered to be opened for public use from the 2022A period. In this subsection, we show research results that visualize the adhesive factor at the adhesive interface between a thermoplastic polymer and a thermosetting epoxy adhesive [5].

We employed polyetheretherketone (PEEK) as a thermoplastic polymer material, which is often used as the matrix material for carbon fiber reinforced plastics (CFRPs), and bisphenol A diglycidyl ether (DGEBA) cured with 4,4’ diamino-diphenyl sulfone (DDS) (DGEBA-DDS) was employed as a thermosetting epoxy adhesive. Since the thickness of the adhesive interface is considered to be several tens of nm, oblique polishing was performed at an inclination angle of 2 degrees so that the interface could be magnified to about a factor of 28.7. Furthermore, to make it easier to observe the vicinity of the interface of DGEBA-

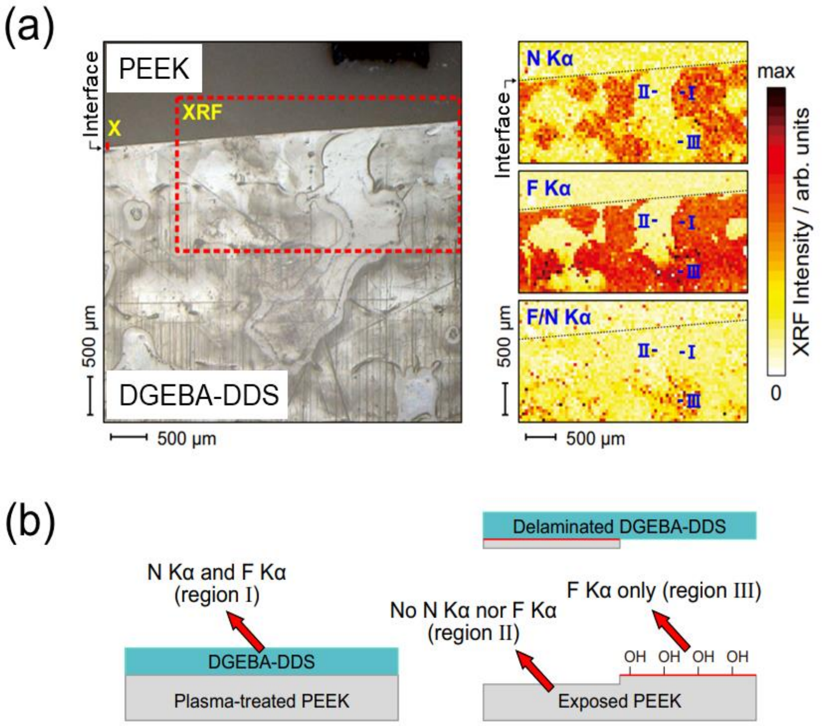

Fig. 2. (a) (Left) Optical microscopy image of DGEBA-DDS/PEEK sample obliquely polished. (Right) N Kα and F Kα images and image representing their ratio recorded at 780 eV. (b) Schematics of adhesion failure determined by microprobe XRF imaging.

DDS/PEEK, a trifluoroacetic anhydride (TFAA) treatment (R-OH → R-$OCOCF_3$) was performed in which the hydroxy (OH) group introduced into PEEK by plasma treatment was fluorinated.

Figure 2(a) shows the elemental distribution maps observed with the SX microscope. The upper map on the right-hand side shows the distribution of nitrogen, the middle map indicates the distribution of fluorine, and the lower map represents their ratio. From these maps, it was found that there were three regions near the adhesive interface of the DGEBA-DDS/PEEK used in this experiment. It was elucidated that these three regions exhibited different adhesive fracture modes. In addition, by performing microprobe XAFS measurements across the interface, it was possible to investigate the change in the chemical state across the interface. We could observe the covalent-bond formation at the interface. We could visualize multiscale phenomena in the adhesion mechanisms, including the sub-mm complex interface structure, the sub-μm distribution of the functional groups, and the molecular-level chemical state distribution. For details, refer to the article [5].

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