

Material analysis end-station of the Hyogo-ken beamline at SPring-8

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Plans to construct surface-analysis equipment which will be placed on beamline BL24XU of SPring-8 are presented. There are three experimental hutches in BL24XU, which are available simultaneously by using diamond monochromators as beam splitters. The purpose of the surface-analysis equipment is the simultaneous measurement of fluorescent and diffracted X-rays in grazing-incidence geometry. The instrument is equipped with a solid-state detector (SSD) and a flat position-sensitive proportional counter (PSPC) combined with analysing crystals for X-ray fluorescence (XRF) analysis. A curved PSPC and the goniometer that mounts the SSD used for XRF are also installed for X-ray diffraction. X-ray fluorescence holography and polarized X-ray emission spectroscopy modes are available, so three-dimensional images of atomic configurations and also the anisotropic structure of materials will be studied.

Keywords: SPring-8; surface analysis; X-ray diffraction; X-ray fluorescence analysis; X-ray fluorescence holography; polarized X-ray emission spectroscopy.

1. Introduction

The beamline BL24XU of SPring-8 (Matsui *et al.*, 1998) will be constructed by Hyogo prefecture in 1998 (Hyogo is the name of the 47 prefectures in Japan, where SPring-8 has been constructed). We call this beamline the Hyogo-ken beamline (ken is Japanese for prefecture). The main purpose of the Hyogo-ken beamline is scientific and technical support for local industries. Three experimental hutches are set up for structural biology, material analysis and medical applications. An in-vacuum figure-8 undulator (Tanaka, 1997) is installed as an insertion device in the Hyogo-ken beamline. Synchrotron radiation beams which are generated by this undulator have high brilliance [1×10^{19} photons s^{-1} $mrad^{-2}$ mm^{-2} (0.1% bandwidth) $^{-1}$] with both horizontal and vertical polarization and are supplied simultaneously to each hutch by means of a diamond monochromator as a beam splitter. In the hutch for material analysis, the incident beam consists of horizontally polarized 9.6 keV photons. We are planning to construct surface-analysis equipment for industrial

applications. This equipment is designed for public use, and the main purpose of this equipment is high-resolution and simultaneous analysis of a material's surface by means of fluorescent and diffracted X-rays.

2. Outline of equipment

Our equipment is schematically shown in Fig. 1. This equipment is designed to analyse elemental composition, chemical states and structures simultaneously. It consists of four major instrumental parts: sample chamber (including sample holder driven with high precision), a solid-state detector (SSD), a curved position-sensitive proportional counter (PSPC) and a flat PSPC combined with an analysing crystal (flat PSPC spectrometer). The basic capabilities of each part are shown in Table 1. The monochromated synchrotron radiation beam of 9.6 keV photon energy is properly collimated by two quadrant slits and introduced to the sample. A PIN photodiode solid-state detector (PIN-SSD) or a flat PSPC spectrometer detects fluorescent X-rays to analyse composition and chemical states of the samples. Measurement of minor elements is possible by means of total-reflection X-ray fluorescence (TXRF) analysis. The PIN-SSD is also used for X-ray diffraction (XRD) analysis since it is mounted on the goniometer. The flat PSPC spectrometer is used for wavelength-dispersive X-ray fluorescence (WDXRF) analysis. The flat PSPC spectrometer is designed to attain any angle with respect to the plane of polarization of the synchrotron radiation beam. The diffracted X-rays in the hemispherical area can be measured, because the curved PSPC can be rotated around the centre of the sample holder. The purpose of this mechanism is to collect diffraction spots and for X-ray fluorescence holography. The configurations of each instrumental part are changed according to XRD, TXRF and WDXRF analysis modes. Fig. 2 shows the relationship of samples, instrumental parts and X-ray beam in each mode of analysis. Each mode of analysis is already used in many synchrotron facilities (see for example, Aulchenko *et al.*, 1995; Chevallier, 1987; Ohashi *et al.*, 1991). However, there is little equipment in which high-resolution or simultaneous measurements can be carried out for each mode of analysis. For example, the effect of X-ray sources on the TXRF was studied by Iida *et al.* (1985). They showed that the use of monochromatic X-ray excitation is most suitable for improving the signal-to-noise value. The fluorescent X-rays from the samples, however, are very weak when a monochromatic X-ray source is used. Therefore, the use of a high-brilliance and monochromatic X-ray beam for TXRF and further high-resolution and simultaneous measurements is needed. In addition, our equipment has two

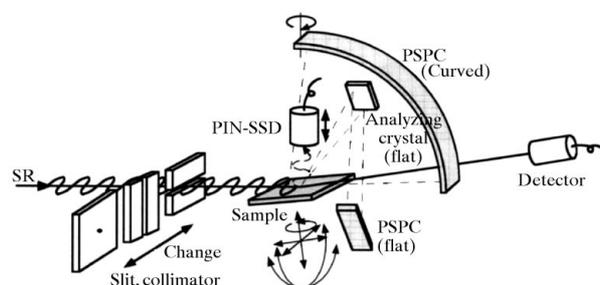


Figure 1 Schematic view of the surface-analysis equipment. SR = synchrotron radiation.

Table 1

Basic capabilities of instrumental parts.

Sample chamber	Vacuum Cleanness Sample stage	<0.05 torr <Class 100 Sample size Accuracy	40 mm × 40 mm × 10 mm x, y: <0.005 mm (−10–10 mm) z: <0.001 mm (−5–5 mm) ω : <0.001° (0–360°) χ : <0.001° (0–90°) φ : <0.05° (0–360°)
PIN-SSD (XRD, TXRF)	Count rate Time constant TXRF mode XRD mode (on goniometer)	40 000 counts s ^{−1} 10 μs Energy range Energy resolution Range Radius Position resolution	2–10 keV $E/\Delta E > 20$ 140° 150 mm <0.01°
Curved PSPC (XRD)	Count rate Range Radius Position resolution Time resolution	100 000 counts s ^{−1} (500 counts s ^{−1} channel ^{−1}) 120° 250 mm <0.08° <5 ms	
Flat PSPC combined with analysing crystals (WDXRF)	Count rate Time constant Energy range Position resolution Energy resolution Distance from sample	40 000 counts s ^{−1} 0.1 μs 2–10 keV <200 μm $E/\Delta E > 2500$ 1400 mm	

main features: (i) X-ray fluorescence holography by means of rotating the curved PSPC, and (ii) high-resolution and polarization analysis of fluorescent X-rays by means of the flat PSPC spectrometer.

3. Features of the equipment

3.1. X-ray fluorescence holography

X-ray fluorescence holography (XFH) is a unique technique for obtaining direct three-dimensional images of atomic configurations (Fadley & Len, 1996). The basic idea of this analysis was suggested by Gabor (1948) and the first excitation experimental result was obtained by Tegze & Faigel (1996). In XFH, observation of a hologram with atom-scale resolution is possible because fluorescent X-rays excited from a single atom are used as the reference wave, *i.e.* a single atom acts as a probe. However, measurement of X-ray intensity profiles which are 0.1% of the total intensity or less is required to detect the hologram through interference between the fluorescent reference X-ray beam and the scattered X-ray beam. Tegze & Faigel (1996) have measured two-dimensional holograms by turning the sample and moving the Ge SSD. Therefore, it is considered that the quality of the measured data was affected by the movement accuracy of the sample and the detector. The two-dimensional hologram can be

measured without moving the samples using our equipment, because X-ray spectra in the hemisphere area can be obtained by rotating the curved PSPC as mentioned above. Thus, it is expected that more precise holograms will be obtained using our equipment.

3.2. High-resolution and polarization analyses

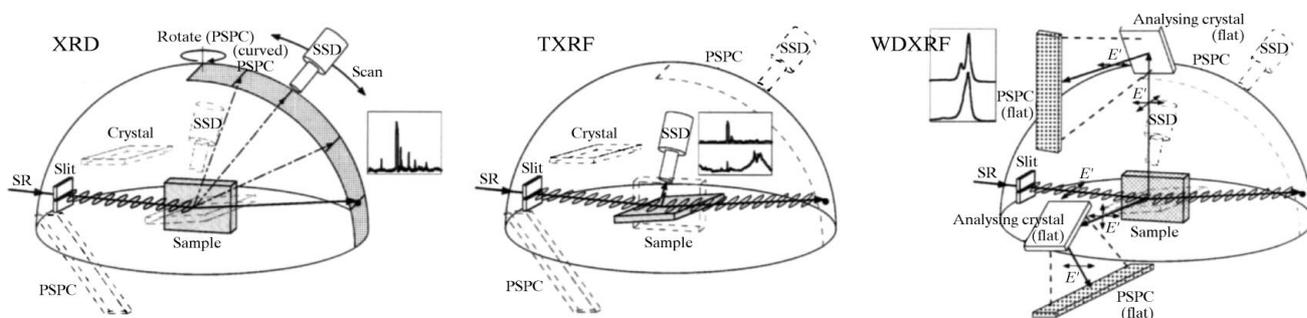
In the case of the PSPC combined with an analysing crystal, the resolution of the fluorescent X-ray spectra is determined by the source size of the fluorescent X-rays, the distance from the sample to the PSPC, the take-off angle and the resolution of the PSPC *etc.* The energy resolution, ΔE , is calculated as

$$\Delta E = E \cot \theta \Delta \theta,$$

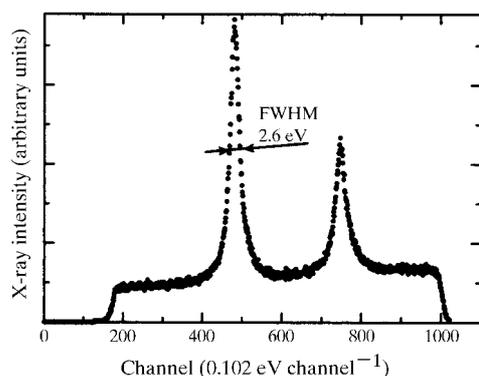
where

$$\Delta \theta \simeq (\Delta \theta_1^2 + \Delta \theta_2^2)^{1/2}, \quad \Delta \theta_1 = D/L, \quad \Delta \theta_2 = S/L,$$

where θ , D , S and L are the take-off angle, X-ray source size, resolution of the PSPC and distance from the sample to the PSPC, respectively. For example, if the fluorescent X-ray source size is 50 μm and an Si(220) crystal is used as the analysing crystal, ΔE is approximately 3 eV for an X-ray energy of 8 keV using our equipment.

**Figure 2**

Relationship of samples, instrumental parts and X-ray beam in XRD, TXRF and WDXRF analysis modes. SR = synchrotron radiation.

**Figure 3**

Ga K X-ray spectrum of GaP wafer [2.5 GeV, 311 mA, Si(008) reflection, sample-crystal 280 mm, crystal-PSPC 710 mm].

Fig. 3 shows a Ga K X-ray spectrum of a GaP wafer measured with a flat PSPC spectrometer on the KEK-PF beamline BL-4A. The size of the incident synchrotron radiation beam was $500\ \mu\text{m} \times 30\ \mu\text{m}$, and the take-off angle was 10° . The energy value per channel was calculated by comparing two peaks with the theoretical value (Bearden, 1969) of Ga $K\alpha_1$ and $K\alpha_2$. The full width at half-maximum (FWHM) was estimated to be about 2.6 eV from this result. The theoretical value of the FWHM of the Ga $K\alpha_1$ line is 2.1 eV (Keski-Rahkonen & Krause, 1974), so it was found that the resolution was sufficient to analyse chemical states using a flat PSPC spectrometer. The capabilities of our PSPC spectrometer are equal to those in BL-4A, so it is expected that a spectrum which is similar to that shown in Fig. 3 can be obtained. In addition, the chemical states of minor elements will be analysed under the condition of total reflection and high-brilliance X-rays using the new equipment.

Recently, polarized X-ray emission spectroscopy (PXES) has been studied by means of third-generation synchrotron sources.

For example, studies of the symmetry of occupied and unoccupied orbitals in randomly oriented samples such as the gas-phase molecule methyl chloride, CH_3Cl , by observing the direction of the X-ray emission polarization has been undertaken (Lindle *et al.*, 1991). Such anisotropic observation of the molecular orbitals is very useful for studying electron or chemical states. In PXES measurements, an incident X-ray beam with a linear polarization is needed for exciting specifically oriented orbitals in randomly oriented samples. With our equipment, the incident X-ray is horizontally polarized and the flat PSPC spectrometer can be set at any angle with respect to the incident X-ray beam, so it is expected that the X-ray emission polarization of molecules, liquid solutions and solids can be measured. PXES has been studied mainly in the soft X-ray region to date. The polarization effect in the hard X-ray region will be measured with the new equipment.

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