Present Status of a New Vacuum Ultraviolet and Soft X-Ray Undulator Beamline BL-13A for the Study of Organic Thin Films Adsorbed on Surfaces

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The present status of a new vacuum ultraviolet/soft X-ray (VUV/SX) beamline (BL-13A) used for the study of organic thin films adsorbed on surfaces is described. The base pressure of BL-13A is maintained below $1 \times 10^{-8}$ Pa in order to prevent contamination of the optics by residual gases. The measured performance is as follows: photon-energy region, $30-1,200$ eV; photon flux, $10^{9}-10^{11}$ photons s$^{-1}$; photon-energy resolution $\langle E/\Delta E \rangle$, 10,000 at a photon energy of 401 eV; spot size (horizontal $\times$ vertical) at the second focus, $=630 \times 120$ $\mu$m; photon-energy drift, $\leq 0.02$ eV at a photon energy of 244.39 eV; reduction of photon flux in the C K-edge region, $\sim 50\%$.

1. Introduction

Recently, organic thin films adsorbed on surfaces have attracted the interest of many researchers. Understanding the structure and electronic properties of the organic-thin-film surface and the film/surface interface is important not only in fundamental science but also in the industry, because of the increasing popularity of organic electronics such as electroluminescent devices and biosensors. To contribute to this field of study, we have constructed a new vacuum ultraviolet/soft X-ray (VUV/SX) undulator beamline (BL-13A) at the Photon Factory (PF) $^{1,2}$.

To carry out in-depth studies on organic thin films by high-resolution X-ray photoelectron spectroscopy (XPS), high-resolution angle-resolved photoelectron spectroscopy (ARPES), and high-resolution soft X-ray absorption spectroscopy (XAS), high photon-energy resolution $\langle E/\Delta E \rangle > 10,000$, high photon flux $> 10^{9}$ photons s$^{-1}$ at $E/\Delta E = 10,000$, and small spot size on the sample (ca. 100 $\mu$m) are required in the 30-700-eV photon-energy region. This region covers the C 1$s$, N 1$s$, O 1$s$, and F 1$s$ absorption edges as well as VUV. The photon-energy region of 700-1,000 eV that involves the few meV$^8$ to improve the stability of the photon energy. This system was first used in BL-28 at PF in 2005, and the achieved photon-energy stability was a few meV$^9$. The 300 and 1,000 lines mm$^{-1}$ VLSGs cover photon-energy regions of 30-330 eV and 100-1,200 eV, respectively. VUV/SX radiation diffracted with the VLSG is monochromatized with S and then refocused by M3 onto the sample position. The advantages of the optics used are as follows:

1) High energy resolution can be achieved for a wide range of photon energies because the included angle is variable, and the grating and the exit slit can be separated by a long distance.

2) High photon flux can be achieved because no entrance slit is placed, and the number of optics used is very small, 4.

2.2 Vacuum system of BL-13A

The carbon contamination of optics exposed to synchrotron radiation (SR) has been a subject of intense study$^{10-11}$. Boller et al. measured the carbon deposition...
proposed the following equation for the contamination rate $K$:

$$K = \frac{C_1 P I}{C_2 P + C_3 \frac{\Delta E}{kT} + I}$$  \hspace{1cm} (1)$$

where $P$ is the pressure, $I$ is the photoelectron current, $T$ is the surface temperature, and $\Delta E$ is the activation energy for thermal desorption. They concluded that the dissociation of adsorbed hydrocarbons, induced by photoelectrons, was responsible for the contamination; these conclusions are consistent with the results reported by other groups. Therefore, hydrocarbon-free ultrahigh vacuum (UHV) is indispensable for suppressing the contamination of the optics. The M1, M2/VLSGs, S, and M3 UHV chambers are made of stainless steel (SS304). In order to suppress outgassing, the inner side of the chambers, as well as the metallic parts (except for bearings and bellows), were polished electronically and rinsed with pure water. The bearings were cleaned with organic solvent. The main pumping components and the base pressures of the chambers are listed in Table 1.

The baking temperature of BL-13A was carefully controlled to avoid thermal damage of the position-adjustment mechanism and the cooling system of the optics. The maximum baking temperature of the M1 and M2/VLSGs chambers was about 90°C, while that for the S and M3 chambers was about 120°C. After a two-week baking period and activation of the non-evaporable getter (NEG) assemblies, the base pressure of each chamber, monitored with cold cathode vacuum gauges (Balzers, IKB060), reached $<1 \times 10^{-8}$ Pa.

Pneumatic valves are placed on the entrance ports of the turbomolecular pumps of the M1, M2/VLSGs, and M3 chambers. These valves close automatically when a power failure takes place. In fact, all of the pneumatic valves closed when the 9.0-magnitude earthquake hit East Japan on March 11, 2011 (the intensity on the Japanese seven-stage seismic scale in the Tsukuba area was 6). When we restored power and turned on the sputtering ion pumps on April 5, 2011, the pressure in every chamber of BL-13A recovered to $\approx 1 \times 10^{-8}$ Pa within a few hours.

### 2.3 Apparatus for monitoring of the photon beam

A UHV chamber (Monitor chamber, Baroque International, Fig. 4) is placed downstream of the M3 chamber to monitor the photon flux and to attenuate higher-order diffraction. The top conflat flange is installed together with three linear feedthroughs. The first one is equipped with Si and Mg filters to attenuate higher harmonics with photon energies of $>98$ eV and $>49$ eV, respectively. These filters are used for photoelectron spectroscopy in the VUV region to suppress signals derived from higher-order diffraction. On the second feedthrough, a gold mesh with a transmittance of 77% and a sapphire plate are attached to monitor the relative photon flux and the photon-beam position, respectively. The same chamber is also furnished with a gold evaporator. On the third feedthrough, a silicon photodiode (International Radiation Detectors, AXUV-100) is mounted to measure the absolute photon flux.

For the estimation of the photon-energy resolution and the calibration of photon energy, another UHV chamber (Calibration chamber, Baroque International, Fig. 5) is connected to the Monitor chamber. On the top conflat flange, a sample manipulator, a sample rod made of highly oriented pyrolytic graphite (HOPG), and a Si
Table 1  Pumping components and base pressures of the chambers in BL-13A. TMP, SIP, NEG, and TSP represent the turbomolecular pump, sputter ion pump, non-evaporable getter, and titanium sublimation pump, respectively. Every TMP is pumped with an oil-sealed rotary pump via a foreline trap. The NEG assemblies of the Monitor and Calibration chambers are fabricated in-house. All of the pumping components were operated normally after the 9.0-magnitude earthquake on March 11, 2011.

<table>
<thead>
<tr>
<th>Chamber</th>
<th>Pumping components</th>
<th>Base pressure [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 chamber</td>
<td>TMP (Edwards, STP–301, 300 L s⁻¹)</td>
<td>&lt;1 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>SIP (ANELVA, 912–7060, 400 L s⁻¹)</td>
<td>&lt;1 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>NEG assembly (SAES getters, GP 50 St707)</td>
<td></td>
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<tr>
<td></td>
<td>NEG assembly (SAES getters, GP 200 MK5 St707)</td>
<td></td>
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<tr>
<td>Monochromator chamber</td>
<td>TMP (Edwards, STP–451, 400 L s⁻¹)</td>
<td>&lt;1 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>SIP (ANELVA, 912–7060, 400 L s⁻¹)</td>
<td>&lt;1 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>Two NEG assemblies (SAES getters, GP 50 St707)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NEG assembly (SAES getters, GP 200 MK5 St707)</td>
<td></td>
</tr>
<tr>
<td>S chamber</td>
<td>TSP (ANELVA, 956–7015)</td>
<td>&lt;1 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>SIP (ANELVA, 912–7020, 110 L s⁻¹)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NEG assembly (SAES getters, GP 50 St707)</td>
<td></td>
</tr>
<tr>
<td>Duct between Monochromator and S chambers</td>
<td>NEG assembly SAES getters, GP 50 St707</td>
<td>&lt;1 × 10⁻⁸</td>
</tr>
<tr>
<td>M3 chamber</td>
<td>TMP (Edwards, STP–301, 300 L s⁻¹)</td>
<td>&lt;1 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>SIP (ANELVA, 912–7020, 110 L s⁻¹)</td>
<td>&lt;1 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>Two NEG assemblies (SAES getters, GP 50 St707)</td>
<td></td>
</tr>
<tr>
<td>Monitor chamber</td>
<td>NEG assembly (SAES getters, St707/CTAM/30D)</td>
<td>2.5 × 10⁻⁸</td>
</tr>
<tr>
<td>Calibration chamber</td>
<td>Tandem TMPs (Leybold, Turbovac 50, 50 L s⁻¹; Balzers, TPU 50, 50 L s⁻¹)</td>
<td>1 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>NEG assembly (SAES getters, St707/CTAM/30D)</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 4](a) Top and (b) side views of the Monitor chamber. (c) Top conflat flange is attached with three linear feedthroughs.

![Fig. 5](a) Top and (b) side views of the Calibration chamber. (c) The end of the sample rod is placed on the top of the sample manipulator on the chamber. HOPG stands for highly oriented pyrolytic graphite.

(111) wafer are mounted (Fig. 5(c)) in order to calibrate the photon-energy scale using the following two resonance peaks: HOPG, C 1s → π*, ℏν = 285.5 eV\(^{13}\); Si (111), Si 2p\(_{3/2}\) → bulk conduction band edge, ℏν = 99.97 eV\(^{14}\). For more accurate calibration, gas inlet for CO\(_2\), N\(_2\), O\(_2\) and noble gases, and an ion detector\(^{15}\) are also provided. The following transition energies can be used as references for the photon-energy calibration: Ar 3s\(^2\) 3p\(^6\) → (3P)3d\(^2\)(2P\(_{3/2}\))4p, 30.848 eV\(^{16}\); Xe 4d\(_{5/2}\) → 6p, 65.11 eV\(^{17}\); Kr 3d\(_{5/2}\) → 5p, 91.20 eV\(^{17}\); Ar 2p\(_{3/2}\) → 4s, 244.39 eV\(^{17,18}\); CO\(_2\), C 1s → 3p, 294.96 eV\(^{19}\); N\(_2\), N 1s \((\nu = 0) \rightarrow \pi^* \ (\nu' = 1), 401.10\) eV\(^{10}\); O\(_2\), O 1s → 3σ\(_g^o\), 539.05 eV\(^{19}\); Xe 3d\(_{5/2}\) → 6p, 674.00 eV\(^{18}\); Ne 1s → 3p, 867.13 eV\(^{20}\); Ne 1s → (3P)3p\(_4\)p, 905.39 eV\(^{21}\).

3. Measured performance of BL-13A

3.1 Photon flux

Figure 6 shows the typical undulator spectra measured...
using a silicon photodiode. On the basis of a series of undulator spectra measured for an undulator gap of 100–210 mm, the photon flux for an exit-slit width of 30 μm is estimated to be $10^{11}$–$10^9$ photons s$^{-1}$ for 30–1,200 eV. The measured photon flux is one order of magnitude smaller than the calculated value, when the acceptance angles are assumed to be 0.4 mrad × 0.2 mrad$^{11}$. The probable causes of the reduced photon flux are the small acceptance angles in the measurements (ca. 0.06 mrad × 0.2 mrad) and contamination of the optics.

3.2 Photon-energy resolution

To estimate the photon-energy resolution ($E/\Delta E$), we measured the X-ray absorption spectrum (XAS) of gaseous N$_2$ in the region of the N 1$s$ → $\pi^*$ excitation using the 1,000 lines mm$^{-1}$ VLSG at the exit-slit width of 30 μm (Fig. 7). The spectrum was fitted using Voigt functions, where the natural lifetime width was taken to be 113 meV$^{18}$. Using the Gaussian width obtained from the curve fitting, $E/\Delta E$ was estimated to be about 10,000 at a photon energy of 401.1 eV. This value is comparable to that for the new soft X-ray beamline BL07LSU constructed for the long undulator SPRing-8$^{22}$ but slightly lower than the designed value ($E/\Delta E \approx 11,500$)$^{11}$. This result suggests that the position of the exit slit is not optimal yet.

3.3 Spot size on the focus

The spot size on the sample position is especially important for microscopic and microspectroscopic applications. The foci of the first and second M3s of BL-13A are located 2 m and 6 m downstream of the M3 position, respectively (see Fig. 1). A typical spot size at the first focus with the second M3, measured by a knife-edge scan, is about 630 × 120 μm (horizontal × vertical) for an exit-slit width of 40 μm$^{11}$. The spot size at the first focus with the first M3 has not yet been measured because of problems with the measurement apparatus. It is expected to be about 210 × 40 μm (horizontal × vertical), because the first and second M3s are 1:1 and 1:3 focusing mirrors, respectively. This size is slightly larger than that designed ($\approx 130 \times 40$ μm (horizontal × vertical)$^{11}$).

3.4 Stability of photon energy

The good stability of the photon energy is indispensable for long-duration measurements at a fixed photon energy. To estimate the stability of the photon energy, we repeatedly performed XAS measurements in the region of the Ar 2p$_{3/2}$ → 4s excitation using the 300 lines mm$^{-1}$ VLSG. Figure 8 shows the plots of the measured photon energies of the Ar 2p$_{3/2}$ → 4s XAS peak as a function of time. The result shows that the drift at $hv = 244.39$ eV is within ±0.02 eV for 400 min.

3.5 Reduction of photon flux in the C K-edge region

Carbon contamination of optics reduces the photon flux in the carbon K-edge region (275–330 eV), and often causes artificial structures in the XAS of organic molecules on a surface. Figure 9 shows the typical photon intensity in the carbon K-edge region. The reduction in the photon intensity at the carbon K-edge region was about 50% at its maximum, suggesting that the optics were contaminated to some degree, since the typical reduction in photon intensity at the carbon K-edge region just after cleaning of the optics is about 15%$^{23}$.

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Fig. 6 Typical undulator spectra measured by a silicon photodiode for (a) 300 and (b) 1,000 lines mm$^{-1}$ VLSGs with an exit-slit width of 30 μm.

Fig. 7 (Color online) X-ray absorption spectrum of gaseous N$_2$ in the region of the 1$s$ → $\pi^*$ excitation, using the 1,000 lines mm$^{-1}$ VLSG for an exit-slit width of 30 μm (solid circles in the upper panel). The solid lines in the upper panel represent the fitting curves using Voigt functions, where the natural lifetime width is taken to be 113 meV$^{18}$. The Gaussian width obtained from the fitting is 39.96 meV. This value corresponds to the photon-energy resolution ($\Delta E$). Thus, the photon-energy resolution ($E/\Delta E$) is estimated to be about 10,000 at a photon energy of 401 eV.

Fig. 8 Measured XAS peak as a function of time. The result shows that the drift at $hv = 244.39$ eV is within ±0.02 eV for 400 min.
4. Conclusions

A new VUV/SX beamline (BL-13A) in the Photon Factory has been open to users in 2010. BL-13A is mainly dedicated to studies on organic thin films by high-resolution ARPES, XPS, and XAS. The base pressure of BL-13A is maintained below $1 \times 10^{-8}$ Pa. The measured performance is as follows: photon-energy region, 30–1,200 eV; photon flux, $10^9$–$10^{11}$ photons s$^{-1}$; photon-energy resolution ($E/\Delta E$), 10,000 at $h\nu = 401$ eV; spot size (horizontal×vertical) at the second focus, ≈630×120 μm; photon-energy drift, $\leq \pm 0.02$ eV at $h\nu = 244.39$ eV; reduction of photon flux in the C K-edge region, about 50%.

The photon flux can be increased by increasing the acceptance angles for the undulator radiation. Photon-energy resolution may be improved by optimizing the position of the exit slit. Carbon contamination of the optics can be reduced by atmospheric-pressure UV/ozone cleaning$^{24}$ or synchrotron-radiation-activated oxygen cleaning$^{25}$. Further commissioning is now underway.

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[References]