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Soft X-ray photochemistry beamline at SPring-8

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Design and construction of a soft X-ray beamline at SPring-8 is reported. The beamline utilizes high-quality linearly polarized soft X-rays obtainable from a figure-8 undulator for the study of photophysical and photochemical processes of atoms, molecules and surfaces in the inner-shell excitation region. It consists of two experimental stations, a photochemistry station and a chemical vapour deposition (CVD) station. A high-resolution grating monochromator is installed at the photochemistry station, while the intense undispersed undulator radiation is used at the CVD station. Unique features of the experimental chambers and of the analysis and characterization systems are described along with those of the monochromator.

Keywords: soft X-ray photochemistry; soft X-ray CVD; inner-shell excitation; high-resolution grating monochromators.

1. Introduction

Although SPring-8 is basically a hard X-ray machine, intense soft X-rays of high quality are also expected to be obtained with this third-generation machine by using undulators of long period length. Such soft X-rays are in great demand in various fields of physics, chemistry and biology. As one of the soft X-ray beamlines planned at the SPring-8 site, we are constructing a beamline that utilizes linearly polarized radiation emerging from the figure-8 undulator (Tanaka & Kitamura, 1995) for the basic study of photophysical and photochemical processes of atoms, molecules and surfaces. Application to material processing in microelectronics is also within its scope. Research subjects using these soft X-rays include: (i) very high resolution molecular spectroscopy; (ii) a perfect experiment on atomic and molecular photoionization dynamics; (iii) complete determination of dissociation pathways and dynamics of inner-shell excited complex molecules; (iv) search and characterization of novel inner-shell excited states of molecules by synchrotron radiation–laser double-resonance techniques; (v) growth of thin films of functional materials; (vi) microfabrication by functional material etching; (vii) elucidation of reaction mechanisms of deposition and processes. To accommodate all these subjects, which have different photon requirements, two experimental stations have been built on two branches of the beamline. Beams are guided into either of the two branches by a horizontally deflecting mirror. One station is called the soft X-ray photochemistry station and accommodates research subjects (i) through (iv), all of which inevitably require a high-resolution monochromator. The other station is called the soft X-ray CVD station and accommodates subjects (v) through (vii). Undispersed undulator radiation is used at this station as the subjects require as high an intensity of soft X-rays as possible. These experimental stations and the monochromator are described in some detail below.

2. Monochromator

As mentioned above, a high-resolution monochromator is essential in the photochemistry branch of the beamline. Resolving power required for our purposes is as high as $E/\Delta E \geq 10\,000$ at a photon energy of $E = 1$ keV. To meet this requirement, a monochromator with a plane varied-line-space grating (VLSG) has been chosen. Light emerging from the entrance slit is converged by a spherical mirror (SM) and focused on the exit slit after being diffracted by a grating. The basic layout of the monochromator is shown in Fig. 1.

To provide monochromatic light in the energy range from 0.2 to 2 keV, three pairs of SM and VLSG are provided. The angle of incidence to the mirror [$k(M_i)$] and half of the deviation angle to the grating [$k(G_i)$] are chosen as 89.2 and 88.2°, respectively, for the first pair ($SM_1 + G_1$) covering the 2.1 keV range, 88 and 87°, respectively, for the second pair ($SM_2 + G_2$) covering the 1.2–0.4 keV range, and 86 and 85°, respectively, for the third pair ($SM_3 + G_3$) covering the 0.5–0.15 keV range. Holographic ion-beam-etched laminar gratings are used as VLSGs because they are expected to have a smaller scattered component in the diffracted light compared to mechanically ruled gratings. All three VLSGs have a groove density of 1200 lines mm^{-1} at the center. The total distance between the entrance and exit slits is approximately 20 m, and the distance between the gratings and the exit slit is 5.5 m. The resolution of the monochromator is estimated by a ray-tracing calculation. It is found to depend strongly on the magnitude of slope error of the mirror and grating surfaces. With an assumed slope error of SM of 0.1″ and widths of the entrance and exit slits of 10 and 2 μm, respectively, the resolving power $E/\Delta E$ is calculated to be 11 000 at 1.2 keV with an output photon flux of 1.6×10^{10} photons s^{-1}, 12 000 at 0.6 keV with a photon flux of 1.1×10^{10} photons s^{-1}, and 18 000 at 0.25 keV with a photon flux of 5×10^{9} photons s^{-1}.

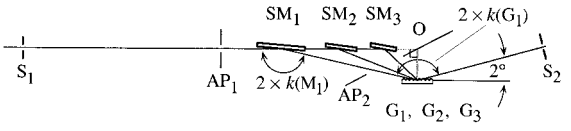

Figure 1
Basic layout of the grating monochromator. S_1: entrance slit; SM_1–SM_3: spherical mirrors; G_1–G_3: varied-line-space gratings; S_2: exit slit; AP_1 and AP_2: apertures. Distances: S_1–O = 14.5 m, G_1, G_2, G_3–O = 0.05 m, G_1, G_2, G_3–S_2 = 5.5 m, S_1–SM_1 = 12.7 m, S_1–SM_2 = 13.8 m, S_1–SM_3 = 14.1 m. $k(M_1)$ and $k(G_1)$ denote the incidence angle to the spherical mirror and half of the deviation angle of the grating, respectively, for the set of $SM_1 + G_1$.

3. Soft X-ray photochemistry station

A schematic drawing of the experimental chambers and analysers of the photochemistry station is shown in Fig. 2. The whole system consists of three major parts: a main chamber to house or attach all the analysers, a chamber for differential pumping (not shown in Fig. 2; it lies to the left of the side view), which also serves as an optical filter chamber for order sorting, and a chamber for main pumping. A reflectron-type time-of-flight mass spectrometer (RTOF) is attached to the main chamber *via* an ICF152 flange. The ionization region, where gases are introduced effusively, is located just in front of the ion inlet of the RTOF. Two ICF203 flange ports are provided to attach a cylindrical mirror electron-energy analyser (CMA). One port is located just opposite the RTOF and allows, when a CMA is attached on this port, coincidence measurements between energy-analysed photoelectron/Auger electron and mass-analysed photoion (PEPICO/AEPICO). The second port is located downstream at a position where a hemispherical electron/ion energy analyser is set inside the chamber. The latter analyser sits on a turntable, which allows the rotation of the analyser around the photon beam axis. In this way, when the CMA is set on this second port, measurements of photoelectron/Auger electron–photoelectron coincidence (PEPECO/AEPECO) and photoelectron/Auger electron–photoion coincidences (PEPICO/AEPICO) are made possible with an additional capability of measuring angular correlation between these two coincident particles.

The whole main chamber can also be rotated around the photon beam axis through an angle of 130°, as shown in Fig. 2. This enables angle-resolved studies of photoelectron/Auger-electron spectroscopy, time-of-flight mass spectrometry, PEPICO/AEPICO and PIPICO spectroscopy, and angular correlation measurements. The rotation can be made with no deterioration of the ultra-high vacuum of the system. This is made manually for the time being but will be switched to an electrically operated system in the near future. For this rotation, the main pumping system for the experimental chamber needs to be separated from the main chamber. The chamber for this main pumping system is seen to the left of the main chamber.

Use of synchronously operated laser and undulator radiation is scheduled in the near future. Incorporation of an electron-energy analyser of still higher energy and angular resolution is also intended.

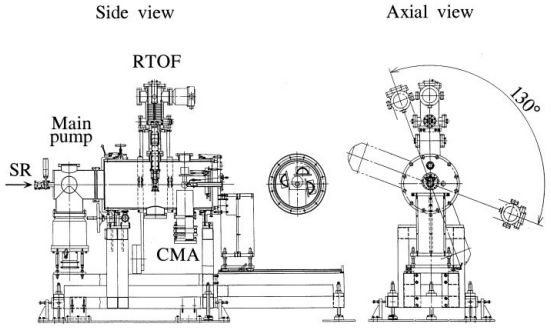

Figure 2
Schematic drawing of experimental chambers and analysers of the photochemistry station. RTOF: reflectron-type time-of-flight mass spectrometer; CMA: cylindrical mirror electron-energy analyser; SR: synchrotron radiation. All pumps are turbomolecular pumps backed by a mechanical pump. Pumping speeds are 1500 l s^{-1} for the main pumping, 260 l s^{-1} for RTOF, and 260 l s^{-1} for three differential pumping ports upstream (not shown in the figure).

4. Soft X-ray CVD station

As mentioned in the *Introduction*, strong soft X-rays from the figure-8 undulator are used without dispersion at this station. When gases of atoms and molecules are irradiated with such high-energy/high-flux soft X-rays, an extraordinarily reactive environment surrounding the substrate can be generated owing to the drastic dissociation of highly excited molecules and the production of various multiply charged ions. Moreover, chemical reaction paths are expected to be controlled by matching photon energy to the dissociation energy of a particular bond, thereby producing a specific reactive species selectively. For this reason, interest in processes such as CVD, surface modification, ablation and etching, induced by such strong soft X-rays, has grown considerably in recent years. Reaction mechanisms of these processes could also be clarified by sophisticated characterization techniques, including *in situ* observation.

The experimental station consists of reaction chambers, analysis instruments and a gas supply/toxic gas treatment system. Reaction chambers actually comprise a high-vacuum reaction chamber, an analysis chamber and a differential pumping chamber. The arrangement of these chambers is shown in Fig. 3. The chambers are desired to be set on a vibrationless bench, so that the position of the specimen to be irradiated is accurately controlled within a few μm. The synchrotron radiation beam from the undulator is split into two by an SiC plane mirror and one part is introduced into the CVD chamber through a differential pumping system. Two types of beam are available at this station: (i) a microbeam, and (ii) a direct beam. The microbeam is generated by focusing the direct beam with two SiC plane-ellipsoidal mirrors. This mirror system is designed so as to give a demagnification of 1/50, and the spot size on the sample is expected to be some tens of μm in both vertical and horizontal directions. On the other hand, the spot size of the direct beam on the sample is several mm in both directions. When irradiation of a larger area is required, a movable stage will be installed to move the substrate in a plane perpendicular to the beam.

An Auger-electron spectrometer (AES) is desired to be installed to obtain *in situ* information on time transients of the chemical compositions of an irradiated specimen surface. Reflected high-energy electron diffraction (RHEED) and Fourier-transform infrared spectrometry (FT-IR) are desired to examine absorbed specimens and to analyse chemical reactions on the surface before/after irradiation, and also to evaluate the crystallinity of formed films. One may need a

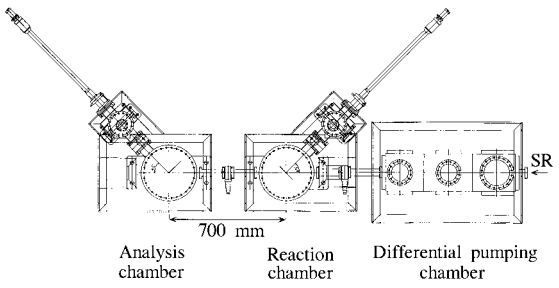

Figure 3
Schematic drawing showing arrangement of three chambers of the CVD station. All pumps are turbomolecular pumps backed by a mechanical pump. Pumping speeds are 500, 500 and 700 l s^{-1} for the three sections of the differential pumping chamber (upstream to downstream) and 500 l s^{-1} for each of the analysis and reaction chambers. SR: synchrotron radiation.

differentially pumped mass spectrometer or particle detection system to estimate chemical reactions during ablation and CVD.

The two-chamber arrangement allows irradiation of solid samples both under ultra-high vacuum conditions and in the presence of added gases. Reaction gases can be introduced into the reaction chamber at pressures up to 1.3×10^2 Pa without deteriorating the ultra-high vacuum upstream. Moreover, a high-density radical-ion source and a *k* cell can be installed to assist reactions. To allow the use of several toxic gases, which is necessary in some CVD and etching studies, a detoxification system that complies with the toxic-gas handling law is installed. A gas-leakage warning system and an automatic shut-off system in the gas supply lines will need to be installed to secure handling of combustible and toxic gases.

References

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