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To cite this article: Yuden Teraoka and Akitaka Yoshigoe 1999 Jpn. J. Appl. Phys. 38 642

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Design of Surface Chemistry End-Station of BL23SU in SPring-8

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(Received October 31, 1998; accepted for publication December 24, 1998)

An experimental apparatus for surface reaction research has been designed as an end-station of a soft x-ray beamline, BL23SU, in the SPring-8. The soft x-ray with intense flux density is provided by a variable-polarizing undulator and is monochromated by using a varied line-spacing plane grating with grazing-incidence. A supersonic molecular beam technique is applied to obtain translational-energy control of incident molecules. Owing to keeping low pressure in the surface reaction chamber during molecular beam operation, the analysis of translational-energy-induced surface reactions is achieved by simultaneous application of the photoelectron spectroscopy. The end-station will promote research activities on new atomic layer reactions induced by the kinetic energy of incident molecules as well as new photofragmentation of monolayer due to the inner-shell selective photoexcitation.

KEYWORDS : SPring-8, soft x-ray, surface chemistry, supersonic molecular beams, photoelectron spectroscopy, photofragmentation

1. Introduction

Progress in surface reaction analyses using molecular beams and charged-particle analyzers, e.g. photoelectron energy analyzer and time-of-flight ion mass spectrometer, has made it possible to investigate chemical reaction dynamics and photofragmentation on solid surfaces. In the surface reaction dynamics, the role of translational and vibrational energy of incident molecules for chemisorption, rearrangement reaction, and desorption is an area of current interest. From an application point of view, the molecular kinetic energy and the photon energy are keys to develop new methods for surface reaction control. The formation of new chemisorption states is expected by irradiation of kinetically-energetic molecules. The photoelectron spectroscopy is very useful to investigate such chemisorbed states. On the other hand, photofragmentation of the chemisorbed states by the inner-shell selective photoexcitation may cause new monolayer formation. In addition, the mass spectrometry of desorbed ions offers information about a photofragmentation scheme. Thus an experimental apparatus for studies of surface reaction dynamics and photofragmentation has been designed as an end-station in a soft x-ray beamline, BL23SU, in the SPring-8. This end-station emphasizes a simultaneous use of supersonic molecular beams and an electron energy analyzer to achieve real "in situ" analysis of surface reactions to obtain more deeper understanding for an elementary process of chemisorption. In this report, the outline of the BL23SU is firstly explained. And then the constitution of the surface chemistry end-station is introduced in detail.

2. Outline of BL23SU

The BL23SU was designed to promote applications of synchrotron radiation in radiobiology, surface chemistry, and especially solid-state spectroscopy of radioactive materials. The beamline is introduced into the radioisotope (RI) laboratory through the experimental hall of the storage ring building. The light source of the beamline (ID23) is referred to as APPLE-II (advanced planar-polarized light emitter), a kind of variable-polarizing undulator. The front-end is constituted by standard components in soft x-ray beamlines of the SPring-8. The beam transport channel components are primarily classified into a soft x-ray monochromator system, RI-protection components, and experimental end-stations.

The ID23 can generate a linearly- (horizontal and vertical plane), an elliptically-, and a circularly-polarized radiation by providing phase shift to the magnet arrays. The most important performance of the ID23 is the switching of right and left circularly-polarized radiation at 0.5 Hz by successful phase-shift driving of the magnet arrays. This feature is expected to promote the study of circular dichroism in spectroscopic research fields.

The grazing-incidence monochromator system consists of a vertically-sagittal-focusing cylindrical mirror, a horizontally-focusing plane mirror with a bending system, an entrance slit, a spherical mirror, a varied line-spacing plane grating, an exit slit, and post-focusing cylindrical and toroidal mirrors. The orientations of pre-focusing mirrors and the grating are controllable by X-terminals through a beamline workstation and a VME system as well as x-ray beam position monitors and XY-slits of the front-end.

End-stations for radiobiology and surface chemistry are installed in the experimental hall of the storage ring building. The other end-station for photoelectron spectroscopy and magnetic circular dichroism studies of

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radioactive materials are installed in the experimental hall of the RI-laboratory. An RI-inspection port, a radiation-measurement chamber with a plastic scintillation detector, a liquid-nitrogen gas-trap chamber, a fast-closing gate valve system had been prepared in the RI-laboratory beamline for RI-protection.

3. Surface chemistry end-station

3.1 Constitution of surface chemistry end-station

General constitution of the surface chemistry end-station is shown in figure 1. The details in each chamber are explained concretely in the following sections. Only brief description is given here. A clean surface is prepared by heating and/or argon-ion sputtering in the surface cleaning chamber. Chemical composition and periodic structure on a single crystal surface are analyzed by low-energy electron diffraction and Auger-electron spectroscopy in the identical chamber. Continuous or pulsed molecular beams are fed into the surface analysis chamber from the supersonic molecular beam chamber. Owing to low pressure during molecular beam operation, an electron energy analyzer is usable. The up-stream beamline is the sixth differential pumping stage from the nozzle chamber caused by doubly-differential pumping in the beam monitor chamber. Thus the pressure in the up-stream beamline is expected to be kept sufficiently low.

3.2 Soft x-ray beam monitor chamber

A synchrotron radiation beam is introduced into the surface reaction analysis chamber through the beam monitor chamber, illustrated in figure 2. The chamber has the following functions: beam shaping by XY-slits, beam intensity attenuation by metal foils, beam position monitoring by a fluorescence screen, absolute beam intensity measurement by a silicon diode (IRD AXUV100), and finally relative beam intensity monitoring by a gold-coated tungsten mesh. These tools except for the XY-slits can be removed from the beam axis by using a linear-motion feedthrough. The chamber is pumped by a hybrid-type turbo-molecular pump (Pfeiffer TMU520) of 300 litter/sec pumping speed. The other pumping unit, which has the same specification as one in the beam monitor chamber, is inserted between the beam monitor chamber and the surface reaction analysis chamber to ensure sufficiently low pressure in the up-stream beamline by differential pumping. In addition, the inserted pump plays a role of differential pumping of two quadrupole mass analyzers and an electron energy analyzer equipped in the surface reaction analysis chamber.

3.3 Preparation chambers

The load-lock and the sample cleaning chambers are indicated in figure 3. It can be kept simultaneously in the load-lock chamber up to eight sample holders. The chamber is evacuated by a hybrid-type turbo-molecular pump (Pfeiffer TMU260) of about 210 litter/sec pumping speed.
installed in the cleaning chamber. The gun is pumped differentially by the turbo-molecular pump of the load-lock chamber. A low-energy electron diffraction equipment with four grids available for Auger-electron spectroscopy (LEED/AES) is also prepared to observe periodic atomic structures on clean surfaces. Auger-electron energy analysis is used to measure chemical composition on surfaces after cleaning. The cleaning chamber is pumped by a hybrid-type turbo-molecular pump (Pfeiffer TMU520) of 500 litter/sec pumping speed.

3.4 Supersonic molecular beam generator

The main parts of the supersonic molecular beam generator are shown in figure 4. Supersonic molecular beams are continuously produced by adiabatic expansion of a mixture of reagent and carrier gases in the first differential pumping stage (nozzle chamber). The beams pass through a skimmer into the intermediate stage (chopper chamber) and finally enter the surface reaction analysis chamber through a shutter and a collimator.

The nozzle chamber is pumped by a 2000 litter/sec magnetically-suspended hybrid-chemical-type turbo-molecular pump (SEIKO STPH2000C). An additional pump of about 200 litter/sec magnetically-suspended hybrid-chemical-type turbo-molecular pump is also used as a backing sub-pump (Pfeiffer TMU400MC). The chopper chamber is pumped by about 1000 litter/sec magnetically-suspended hybrid-chemical-type turbo-molecular pump (Pfeiffer TMU1600MC).

The nozzle tube was made of a pyrolytic boron nitride (PBN). The nozzle orifice diameter is 100 μm. The PBN tube can be heated up to about 1700 K by a pyrolytic graphite heater sandwiched with PBN. A tantalum ribbon is fastened round the PBN heater for convenience of nozzle temperature measurement with a pyrometer. The beam skimmer has a 1 mm diameter hole in its summit and is located about 5 mm downstream from the nozzle orifice. The length is controllable with an XYZ stage outside the nozzle chamber. The gas pipe attached to the nozzle and the skimmer are cooled by running water to prevent severe corrosion by reaction with chlorine gas.

A rotating wheel (chopper) with slits is set inside the chopper chamber. The rotation is driven by a dc motor set outside the chamber. The rotatiounal motion is transferred though a feed-through using magnetic-fluid vacuum seal. The flight length from the orifice to the sample surface is 645 mm. The diameter of the final collimator is 5 mm so that the collimated beams produce 7.3 mm diameter spot on the sample surface.

The translational energy of reagent molecules depends on the mass of the carrier gas, the gas mix ratio, and the nozzle temperature. The upper limit of incident translational energy is expected to be about 5 eV in the case of chlorine molecules. The beam flux will be estimated from the total pressure increase in the reaction analysis chamber due to beam incidence, the pumping speed for the reagent gas, the beam spot area, and the molar ratio of the reagent gas and the carrier gases. The molar ratio is measured with a differentially-pumped quadrupole mass spectrometer equipped in the surface reaction analysis chamber. Under typical operating conditions, the flux density of chlorine molecules in the seeded molecular beams is expected to be about $10^{13}$ molecules/cm$^2$/sec on the sample surface in a continuous beam operation mode.

The chopper is used to measure a mach number of the supersonic molecular beams and also useful for a gas dose control. Typical rotation speed is 1000 to 3000 rpm. Wide slit enables to obtain a continuous beam operation. The motor is installed outside the chopper chamber in order to avoid corrosion by the chlorine gas.

![Fig. 4. Details of the nozzle chamber (left) and the chopper chamber (right). The reagent gas is directly carried into the PBN nozzle. The gas pipe attached to the nozzle and the skimmer are cooled by running water. The rotation of chopper is driven by a dc motor outside.](image)

3.5 Surface reaction analysis chamber

The inner part of the surface reaction analysis chamber is illustrated in figure 5. The surface reaction analyses are achieved by using x-ray photoelectron spectroscopy, temperature-programmed desorption, time-of-flight ion mass spectrometry, electron-ion coincidence measurement, and reactive molecular beam scattering method.

The reaction chamber is evacuated by about 1000 litter/sec magnetically-suspended hybrid-chemical-type turbo-molecular pump (Pfeiffer TMU1600MC) with a backing sub-pump of about 200 litter/sec magnetically-suspended hybrid-chemical-type turbo-molecular pump (Pfeiffer TMU400MC). The chamber is annealed in its fabrication process up to 1350 K in vacuum to reduce out-gas from the chamber wall and a residual magnetic field. The base pressure is expected to be less than $2 \times 10^{-8}$ Pa. The electron energy analyzer (Omicron EA125 with 5 channeltrons) is also evacuated differentially by the turbo-molecular pump of the soft x-ray beam monitor chamber. The quadrupole mass analyzer (Balzers QMS200) for detection of molecular
beams is also differentially pumped by a hybrid-type turbo-molecular pump (Pfeiffer TMU065). The other quadrupole mass analyzer (Balzers QMG421C) for temperature-programmed desorption and reactive molecular scattering measurement is evacuated double-differentially by the turbo-molecular pump of the soft x-ray beam monitor chamber for the intermediate stage and by a hybrid-type turbo-molecular pump (Pfeiffer TMU065) for the analyzer stage. An x-ray source (Omicron DAR400) is equipped for convenience. An electron flood gun is prepared for preventing charge build-up on the sample surface.

![Diagram of surface reaction analysis chamber](image)

**Fig. 5.** Arrangement of the surface reaction analysis chamber, the electron energy analyzer, and the chopper chamber. Synchrotron radiation (SR) comes from upper side in this figure. Emitted electrons are detected during molecular beam operation. Scattered and desorbed molecules are observed by a double-differentially pumped quadrupole mass analyzer. The molecular beams are detected by the other differentially-pumped quadrupole mass analyzer drawn in the right-hand side.

3.6 Gas supply and exhaust system

In order to keep safety in handling toxic halogen gases and flammable gases, e.g., organometalals, a cylinder cabinet, a gas mixer and an exhaust gas treatment system are prepared in combination with the end-station. Chlorine and trimethylgallium are selected as reagent materials in the first stage. The chlorine is supplied as a diluted gas by helium and/or argon. The trimethylgallium is fed by bubbling and heating. The flow rates of chlorine-containing gas and carrier gases are controlled individually by using mass-flow controllers in the gas mixer. The mixed gas is fed into the PBN nozzle. The molecular beams are typically generated at a 0.1 to 0.5 MPa stagnation pressure. The exhaust gas from rotary pumps of the end-station is treated by an adsorption cell. An emergency treatment equipment for gas leak in the cylinder cabinet and the gas mixer is also prepared in this system.

4. Research subjects

The mechanism of surface reactions on semiconductor materials must be understood for developing more precise surface micro-fabrication. The importance of kinetic energy of incident molecules in chemisorption has been shown in the previous reports for Si(100) and poly-Si with chlorine molecules, Si(100) with chlorine atoms. These reactions has been studied by using supersonic seeded chlorine molecular beams and a high temperature nozzle, and examined the translational energy dependence of the reaction yield. The reaction yield was clearly appeared when the translational energy of chlorine molecules was increased to several eV. The role of translational energy and thermal energy in an overall surface reaction was investigated by measuring the temperature dependence of translational-energy-induced reaction. A reaction model, that is, forced chemisorption followed by thermal desorption of chlorinated silicon molecules, was presented for the translational-energy-induced reaction in the Cl2/Si(100) system. However, what happens on a silicon surface during the translational-energy-induced reaction is not still understood well.

SiCl₂ molecules are thermal desorption products under surface temperature of 870 K. Single chlorinated silicon atoms shares on the Si(100) surface. Doubly-chlorinated silicon formation is considered to be a trigger of SiCl₂ desorption. The translational-energy-induced reaction occurs even in low surface temperature at which the SiCl₂ can not desorb. This fact produced a speculation of the "forced chemisorption", that is, triply-chlorinated silicon molecules formation. The formation of the triply-chlorinated silicon molecules should be observed by photoelectron spectroscopy as chemical shifts of the silicon photoelectron peak. Simultaneous irradiation of supersonic molecular beams and high resolution synchrotron radiation enables us to investigate what happens on the surface. Research fields on new surface reactions induced by the kinetic energy of incident molecules as well as new surface photofragmentations caused by the soft x-ray inner-shell selective excitation will be promoted in this surface chemistry end-station.

**References**