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A beamline for photochemical processes at atmospheric pressure

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A beamline especially designed for atmospheric photochemical reactions has been constructed at the NTT synchrotron radiation facility. By inserting a buffer helium chamber with Be and Si_3N_4 partition windows between the beamline and the reaction chamber, studies can be performed without the differential pumping systems normally used in existing photochemistry beamlines. The reaction chamber is equipped with a gas supply system and analysis systems to investigate gas-phase and surface reactions. Purging using dry purified gases in combination with water-bubbling gives effective control of water concentration in the reaction chamber.

Keywords: X-rays; beamlines; photochemical reactions; atmospheric reactions.

1. Introduction

Photochemical reactions in the atmosphere are closely related to basic environmental research in areas such as air pollution, ozone-hole generation, nitrogen or carbon dioxide fixation *etc*. The basic photochemical processes in these fields include photolysis of molecules, generation of free radicals and photocatalytic reactions in solution. Results from research on photochemistry at atmospheric pressure will be applied to developing new material-synthesis technologies from high-pressure gas, liquid and sol–gel sources.

In the field of synchrotron-radiation-induced photochemistry, many studies using reaction gases at low pressures (< 0.1 torr) have already been reported. In existing test equipment, a differential pumping system must be mounted within the beamline to prevent the reactants from flowing into the synchrotron radiation ring and to protect the optical elements from contamination. Because the upper limit of the total pressure in a reaction chamber is, at most, 1 torr for the reasons mentioned above, experiments at higher pressures are difficult with differential pumping. Given this background, we have designed and constructed a special beamline for photochemical reactions in order to realize such experiments at pressures up to atmospheric pressure.

The main purpose of the beamline is to conduct feasibility studies on the synchrotron-radiation-induced production of industrial materials from reactions in gas mixtures at atmospheric pressure, and from reactive or catalytic liquid-phase sources. The products will include materials for not only semiconductor fabrication (Utsumi *et al.*, 1998), but also biochemical industries. In this paper, we will demonstrate the basic concept and the construction of the beamline, and present a method of reducing the concentration of residual water molecules in the reaction chamber to achieve the well defined experimental conditions.

2. Construction of the beamline

The beamline discussed herein has been constructed at the normal-conducting acceleration ring (NAR) at the NTT synchrotron radiation facility (Shibayama *et al.*, 1989). The concept of the beamline design is based on X-ray lithography (XRL) beamlines for exposure in the atmosphere. In these kinds of beamlines, beryllium windows are widely used to separate the beamline and the end-station in air (Oertel *et al.*, 1989). An outline of the optical system of the beamline ABL-5C in NAR is shown in Fig. 1 (Kaneko *et al.*, 1989). The synchrotron radiation beam from NAR is extracted with a horizontal beam divergence angle of 30 mrad, and focused by using a first toroidal mirror (M1) with a beam incident angle of 2.1°. The reflected beam is focused on a point between M1 and a second toroidal mirror (M2). The diverging beam is collected by M2 with an incident angle of 1.5° and collimated to yield a parallel beam. Fig. 2 shows the calculated synchrotron radiation spectrum after reflection by the two toroidal mirrors, M1 and M2. The collimated beam passes through the helium buffer chamber before terminating in the reaction chamber. At the beam entrance of the helium buffer chamber, a 10 × 30 mm beryllium window, 25 μm in thickness (the transmittance of this window is shown in Fig. 3*a*) is mounted to transmit the X-ray component of the beam while separating the high-vacuum beamline from the atmospheric-pressure helium gas. The helium buffer chamber is required to protect the beryllium film from degradation; oxygen gas easily reacts with beryllium under synchrotron radiation irradiation forming toxic beryllium oxide. The beam transmitted through the helium buffer gas is introduced to the reaction chamber without intensity attenuation. At the beam entrance of the reaction chamber, a silicon nitride partition window (20 × 20 mm, 2 μm in thickness; transmittance of this window is shown in Fig. 3*b*) is mounted to separate the helium buffer chamber from the reaction chamber. After passing through the beryllium and the silicon nitride windows, the low-energy component of the beam is eliminated as shown in Fig. 3. As a result of the inclusion of the absorption effect of the windows and the helium gas in the synchrotron radiation spectrum calculation, the photon energy of the beam introduced into the reaction chamber ranges from 1000 to 1800 eV, as shown in Fig. 4.

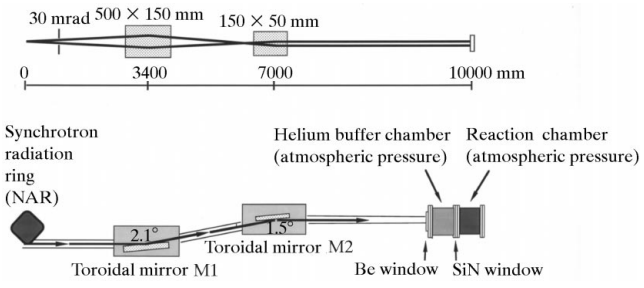

Figure 1
Outline of the beamline ABL-5C, and the optical system.

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Fig. 5 shows a schematic view of the helium buffer chamber and the atmospheric reaction chamber. The gas supply system contains mass-flow controllers with high accuracy and a turbo-molecular pump to evacuate the gas lines and the chambers. The reaction chamber is equipped with analysing systems to investigate gas-phase reactions, such as a quadrupole mass spectrometer for atmospheric pressure (AP-QMS), a stereoscopic optical microscope, a gas micro-analyser with chemiluminescence and pulsed fluorescence detection systems, *etc*. In order to analyse compounds on sample surfaces and molecules in the gas phase, a Fourier-transform infrared spectrometer (FT-IR) is attached. In this spectrometer, a multiple-reflection optical path is used for high spectral resolution.

3. Reduction of residual water

Residual water in the reaction chamber or water-related radicals adsorbed on the inner walls drastically affect the experiments. In reaction chambers which can be evacuated by using pumps, thermal processing is widely used, such as baking of the chamber walls using heaters and sample-surface cleaning using high-temperature flashing. In our experimental apparatus, however, thermal processing methods cannot be used because the silicon nitride window is bonded to the chamber flange using epoxy resin. To resolve this problem, we adopted a purging process: dry pure nitrogen gas or pure air is passed through the gas-feed line into the reaction chamber. The efficiency of the purging process, *i.e.* the quantity of the residual water, was measured with the AP-QMS. Fig. 6(*a*) shows the mass spectrum of the atmosphere in the reaction chamber before purging. As shown in the figure, the

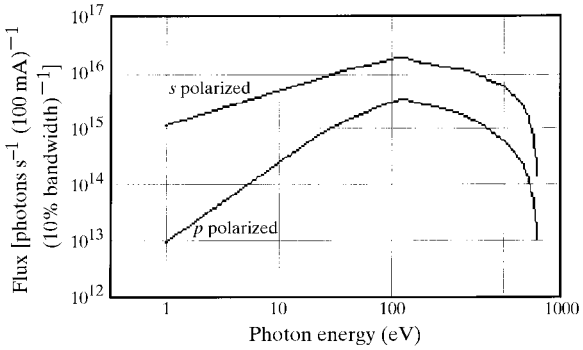

Figure 2
Synchrotron radiation spectrum of the beamline after reflection by the two toroidal mirrors, M1 and M2.

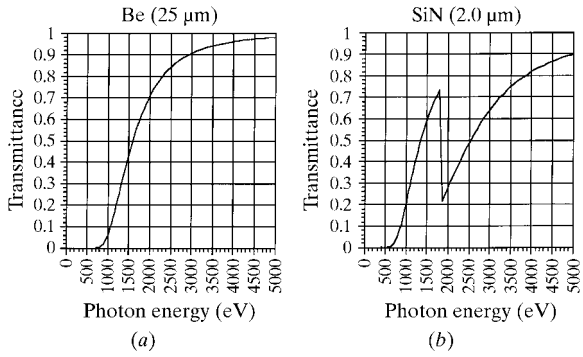

Figure 3
Transmittance of (*a*) the beryllium window and (*b*) the silicon nitride window used in the beamline.

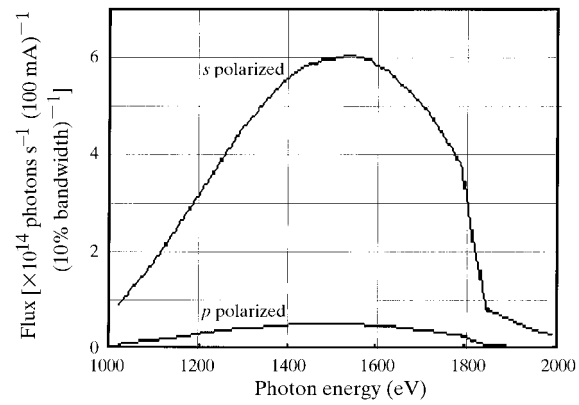

Figure 4
Synchrotron radiation spectrum of the beamline after transmission through the two X-ray windows.

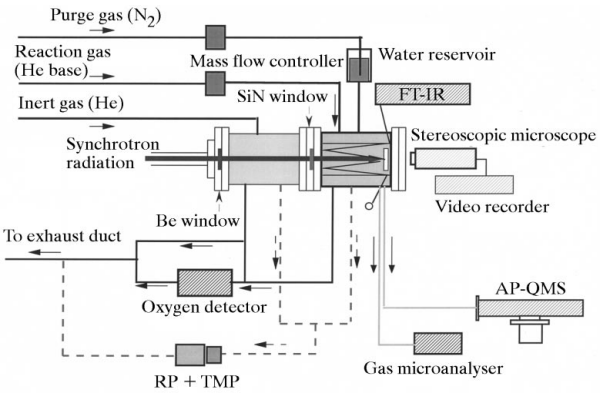

Figure 5
Schematic view of the helium buffer chamber and the reaction chamber. RP = rotary pump; TMP = turbo molecular pump.

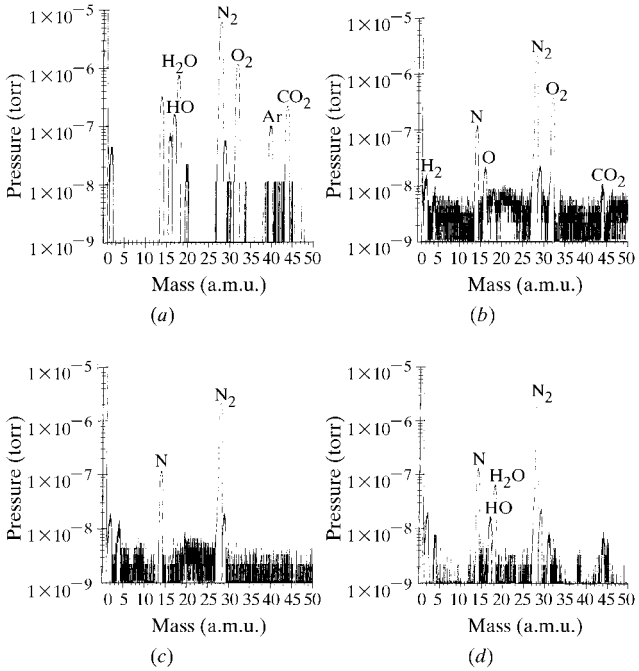

Figure 6
Mass spectra of the atmosphere in the reaction chamber: (*a*) without purging process, (*b*) after purging by pure air, (*c*) after purging by pure nitrogen gas, and (*d*) after adding water to nitrogen by gas bubbling.

peak height of the water signal (m/e = 18) in the reaction chamber is several percent of the signal for air (m/e = 28 and 32). Figs. 6(*b*) and 6(*c*) show the mass spectra of the atmosphere in the reaction chamber after purging by pure air and by pure nitrogen gas, respectively. The water signal has been reduced below the detection limit. This result shows that pure gas purging effectively eliminates the residual water in the reaction chamber.

After the residual water is removed, water concentration in the reaction chamber can be controlled by mixing the reaction gas and water using a water-bubbler which is inserted between the gas-feed line and the gas inlet of the reaction chamber. Fig. 6(*d*) shows the mass spectrum of the atmosphere in the reaction chamber after flowing nitrogen gas is mixed with water by using the bubbler. As shown in the figure, water can be intentionally added into the reaction region.

4. Summary

A beamline especially designed for synchrotron-radiation-induced reactions under atmospheric pressure has been constructed without using differential pumping systems. The pure gas purging and water-bubbling combined with analysing systems allow for control of water concentration in the reaction chamber.

By using the reported technical approach, synchrotron-radiation-induced photochemistry will be feasible not only for inorganic materials synthesis, but also for organic or biochemical materials synthesis, such as artificial photosynthesis, genetic engineering *etc*.

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References

Kaneko, T., Itabashi, S., Saitoh, Y., Toshihara, H. & Kitayama, T. (1989). *Jpn. J. Appl. Phys.* **28**, 2080–2083.

Oertel, H., Huber, H.-L. & Schmidt, M. (1989). *Rev. Sci. Instrum.* **60**, 2140–2143.

Shibayama, A., Kitayama, T., Hayasaka, T., Ido, S., Uno, Y., Hosokawa, T., Nakata, J., Nishimura, K. & Nakajima, M. (1989). *Rev. Sci. Instrum.* **60**, 1779–1782.

Utsumi, Y., Takahashi, J. & Hosokawa, T. (1998). *J. Synchrotron Rad.* **5**, 1141–1143.