X-ray photoelectron spectroscopy under ambient pressure conditions

X-ray photoelectron spectroscopy (XPS) is a powerful tool for measuring the physical and chemical properties of surfaces. A conventional photoelectron spectroscopy analyzer can only operate under high vacuum. One of the reasons for this is that the discharge of the analyzer occurs at low vacuum and the other reason is that the number of photoelectrons decreases quickly when photoelectrons pass through the gas atmosphere because of the electron scattering by gas molecules. Attempts to perform XPS measurement in a gas atmosphere began in the early 1970s. In several cases, differential evacuation was performed between the electron energy analyzer and the sample to prevent the gases from entering the analyzer and to maintain the vacuum under which the analyzer can be operated safely. In addition, a short working distance (WD) between the sample surface and the detector orifice (aperture) was adopted to prevent electrons from passing through a long distance in the high-pressure region. This technique is known as ambient pressure X-ray photoelectron spectroscopy (AP-XPS) [1].

The AP-XPS technique has advanced with the use of third-generation synchrotron radiation light sources. High brightness and small focused beams have allowed the diameter of the aperture to be reduced. Furthermore, by introducing an electron lens into a differentially pumped chamber to increase photoelectron transmission, it has become possible to lengthen the chamber and exhaust residual gases with numerous pumps. These techniques can increase the working pressure in the measurement chamber to 3000 Pa, close to the saturation vapor pressure of water at room temperature. In recent years, AP-XPS has been used in various research areas such as solid-gas reactions, solid-liquid interfaces, fuel cells, and batteries. However, the upper limit of the working pressure is about 3% of atmospheric pressure. Considering that many practical chemical reactions occur under atmospheric pressure or higher, it is desirable to further increase the pressure limit in AP-XPS.

The key requirements for increasing the pressure limit in AP-XPS are a high-brightness light source, a small focused beam, a small aperture, a short WD, and high-energy photoelectrons generated by a high-energy excitation light. Using a small aperture to increase the pressure limit in AP-XPS has two advantages. First, it can prevent gases from flowing into the analyzer, and second, it can shorten the WD without decreasing the actual pressure at the sample surface. Regarding the inflow of gases, we investigated the pressures at a differentially pumped chamber and an analyzer chamber during XPS measurement under atmospheric pressure for apertures of various sizes. We found that an aperture diameter of ≤70 μm can maintain the gaseous pressure in both chambers at a value allowing the spectrometer to be operated safely during the measurement at atmospheric pressure. Concerning such a short WD, the number of photoelectrons with a kinetic energy of 8 keV is decreased to ~0.3% as a result of scattering at nitrogen molecules when they pass through a distance of 60 μm in the atmospheric pressure region. Therefore, a WD close to this value is required in AP-XPS measurement at atmospheric pressure to detect signals with sufficient intensities. The actual pressure at the sample surface, however, may differ from the apparent value measured far from the aperture if the aperture is too close to the sample. Previous AP-XPS experiments suggested that the WD should be twice the aperture diameter in order not to perturb the gas environment at the sample surface. Namely, it is necessary to use an aperture with a diameter of 30 μm to set the WD to 60 μm.

The AP-XPS measurements were conducted at SPring-8 **BL36XU** beamline [2]. Excitation light of 7.94 keV focused to a beam size of 20 μm × 20 μm was used. An AP-XPS system with a commercial differential pumping-type spectrometer (R4000 HiPP-2, Scienta Omicron Inc.) was installed in the beamline [3]. The equipment comprises a pre-lens in a differentially pumped chamber evacuated with several vacuum pumps and a standard hemispherical electron energy analyzer. The standard aperture

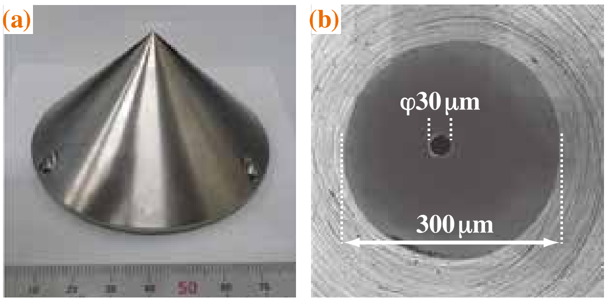

Fig. 1. **(a)** Front cone of the electron energy analyzer. **(b)** Scanning electron microscope image of the aperture shape at the top of the front cone.

at the top of the front cone in the spectrometer has a diameter of 300 μm. In this report, we replaced the front cone with our custom-made one with an aperture diameter of 30 μm, which was shaped by focused ion beam processing, to increase the pressure limit in the AP-XPS measurement (Fig. 1).

We measured the XPS spectra of a Au(111) surface grown on a mica substrate with a WD of 60 μm under various gas pressures using the AP-XPS equipment [4]. The signal intensity obtained by the spectrometer with the 30 μm aperture was ~5% of that obtained with the 500 μm aperture due to the small acceptance angle. Figure 2 shows the intensity decay of the Au 4*f* spectra with increasing gas pressure from 1 Pa to 100 kPa. Here we use 100 kPa as atmospheric pressure. The XPS measurement was not affected by the ambient gas at a pressure of 1 Pa. As the gas pressure increased, the signal intensity decreased because the photoelectrons were scattered by the ambient gas while passing through the sample to the detector. Although the signal intensity was very weak, the appearance of the $4f_{7/2}$ peak was confirmed at atmospheric pressure. The attenuation of the signal from its signal level at 1 Pa was 0.5% at 100 kPa. However, the signal-to-noise ratio can be improved by increasing the acquisition time. Figure 3 shows the Au 4*f* spectrum recorded at atmospheric pressure. The $4f_{7/2}$ and $4f_{5/2}$ peaks can be clearly observed in the spectrum. The Shirley background was subtracted from the spectrum, and the plots were fitted with a Voigt function. The curve-fitting result shows that the energy difference between the $4f_{7/2}$ and $4f_{5/2}$ peaks is 3.7 eV and the intensity ratio $4f_{7/2}$:$4f_{5/2}$ is approximately 4:3. These values are in good agreement with the standard values for Au 4*f* peaks. Thus, accurate photoelectron spectroscopy measurement is possible even under atmospheric pressure using a differential-pumping-type photoelectron spectrometer with an aperture of 30 μm.

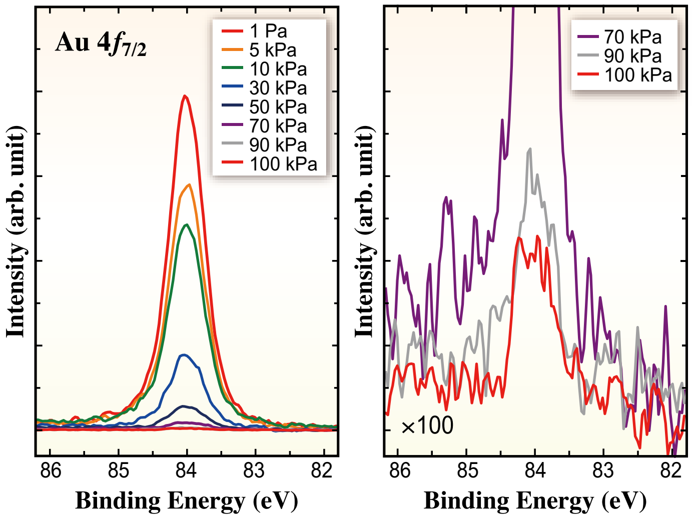

Fig. 2. Au $4f_{7/2}$ spectra recorded using 7.94 keV X-rays at pressures of 1 Pa to 100 kPa. Each spectrum was recorded in an acquisition time of 10 min.

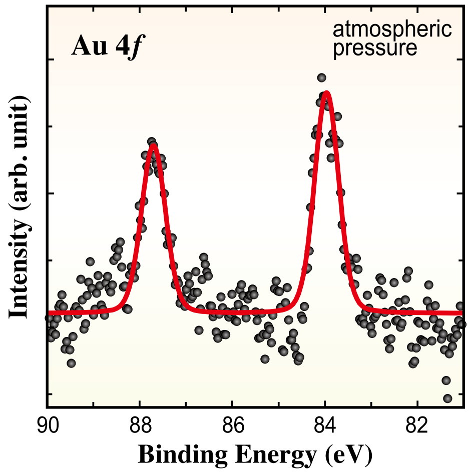

Fig. 3. Au 4*f* spectrum recorded at atmospheric pressure in an acquisition time of 30 min.

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