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Development of Ambient Pressure Hard X-ray Photoelectron Spectroscopy at SPring-8

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An ambient pressure photoelectron spectroscopy measurement that uses with hard X-rays (AP-HAXPES) were conducted at the BL36XU of SPring-8. The AP-HAXPES system with a commercial differential pumping-type spectrometer (R4000 HiPP-2, Scienta Omicron Inc.) was installed in the beamline with the excitation light of 7.94 keV focused to a beam size of 20 μm × 20 μm on the sample position. In this report, we replaced the front cone with our home-made one with an aperture diameter of 30 μm to increase the pressure limit in the AP-HAXPES measurement, although the standard aperture size in the spectrometer is a diameter of 300 μm. In addition, we have adopted the working distance of 60 μm in order not to perturb the gas environment at the sample surface. Using the windowless electron spectrometer system, we have succeeded in measuring X-ray photoelectron spectra under real ambient atmosphere (10^5 Pa).

1. Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful tool for measuring surface physical properties; however, the application of XPS at elevated pressures is complicated because a high vacuum is required for the spectrometer. There are two factors in the difficulties encountered in XPS measurements under high pressures. One is the necessity of low pressures in the electron energy analyzer to avoid discharges on the electrostatic lens elements and the detectors; the other is attenuation of photoelectrons through the gases in the measurement chamber. The first factor was overcome through the use of a long differential pumping system with a small aperture to reduce the molecular flows into the analyzer, whereas the latter was overcome through the use of a shorter working distance (WD) between the sample surface and the detector orifice.

A new AP-HAXPES apparatus equipped with a differential pumping system was constructed at the undulator beamline BL36XU of SPring-8 using excitation light of 8 keV focused to a beam size of 20 × 20 μm^2. we adopted an aperture diameter of 30 μm to reduce gases from entering the analyzer and to maintain a vacuum safe for operating the analyzer. In addition, a WD of 60 μm is adopted to prevent electrons from passing through a long distance in the high-pressure region. The Au 4f spectra from the Au(111) surface were measured by increasing the working pressure of air from 1 to 10^5 Pa. As a result, we demonstrated that the instrument is capable of measuring the photoelectron spectrum under atmospheric pressure. In addition, XPS measurements were applied to insulator samples under a gas atmosphere.

2. Result and Discussion

2.1 Performance of Real Ambient Pressure HAXPES System

The AP-HAXPES measurements were conducted at the BL36XU beamline in SPring-8 [1]. In this report, the excitation light of 7.94 keV was used in the measurements. A commercial differential pumping spectrometer (Scienta Omicron R4000 HiPP-2) comprises a prelens in a differentially pumped chamber evacuated with several vacuum pumps and a standard hemispherical electron energy analyzer. We used the home-made front cone with an aperture diameter of 30 μm prepared using a focused ion beam (Fig. 1(a)).

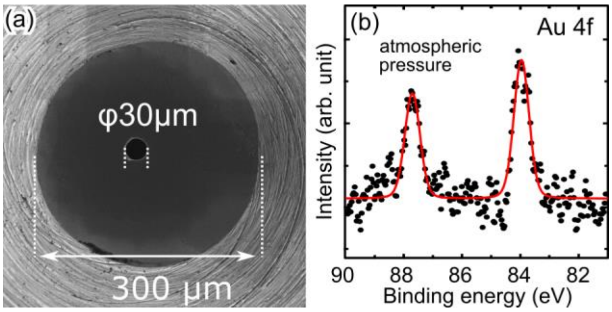

Fig. 1 (a) Scanning electron microscopy image of the aperture prepared at the top of the front cone. (b) Au 4f spectrum recorded at atmospheric pressure in an acquisition time of 30 min. Reproduced from Ref. 2 with modification. Copyright 2017 The Japan Society of Applied Physics.

We measured the XPS spectra of the Au(111) surface grown on a mica substrate under various gas pressures using the AP-HAXPES equipment. In order to maximize the photoemission signal, the incident angle was set to 0.59°. The value is close to the critical angle of gold for 8 keV photons (0.55°). Figure 1(b) shows the Au 4f spectrum at atmospheric pressure. The $4f_{7/2}$ and $4f_{5/2}$ peaks are clearly found 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 that the intensity ratio $4f_{7/2}$:$4f_{5/2}$ is almost 4:3. These values are in good agreement with the standard values of the Au 4f peaks [2].

2.2 XPS measurement for an insulator sample

The ordinary XPS measurement cannot measure the insulator sample because of the charge up of the sample by the emission of photoelectrons. However, for the sample under a gas atmosphere, the ambient gas ionized by synchrotron radiation compensates the charge up of the sample. Using this fact, the AP-HAXPES can obtain the spectrum of insulator samples under a gas atmosphere. For example, figure 2 shows the F 1s spectra of the calcium fluoride, which is a typical insulator. At low ambient pressure, the peak is shifted to a higher energy side, and the spectrum shape is also strange with the shoulder peak at higher energy side. As the pressure increase, the peak move to the correct position. The shape and position of the peak do not change above 30 kPa. This result means that the charge up effect is fully compensated at a pressure of 30 kPa. In this way, photoelectron spectroscopy can be applied to insulator samples under high gas pressure conditions.

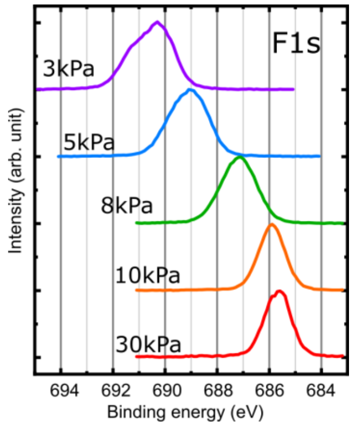

Fig. 2 F 1s spectra of the calcium fluoride at the N_2 gas pressure from 3 kPa to 30 kPa.

3. Conclusion

AP-HAXPES measurements were carried out using the differential-pumping spectrometer with an aperture diameter of 30 μm using excitation light of 7.94 keV focused to a beam size of 20 × 20 μm^2 on the sample surface and by adopting a working distance of 60 μm. The Au 4f spectra of the Au(111) surface were successfully obtained under atmospheric pressure. Under a gas atmosphere, the AP-HAXPES can measure the correct spectrum for insulator sample without peak shift because the photoelectrons coming from the ambit gas molecules compensate the charge up of the sample.

4. Acknowledgement

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5. References

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