

A HAXPES measurement system up to 15 keV developed at BL46XU of SPring-8

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Abstract. In order to achieve much larger probing depth than the conventional HAXPES system of BL46XU, a HAXPES measurement system equipped with a cylindrical sector analyzer, Focus HV-CSA 300/15 has been developed, by which photoelectrons with the kinetic energy up to 15 keV can be analyzed. The Si 1s peak which comes from the buried Si wafer underneath the 60 nm SiO₂ thin films can be clearly identified in the spectra excited by the photon energy of 14 keV, indicating the much larger probing depth than the conventional HAXPES measurement with 8 keV X-ray. The total energy resolution estimated from the Au Fermi edge spectra was ~0.5 eV, which is sufficient for the chemical state analysis of materials.

1. Introduction

In BL46XU of SPring-8, a hard X-ray photoemission spectroscopy (HAXPES) measurement system equipped with an electron energy analyzer, VG Scienta R4000-10 keV, has been installed since 2008, by which photoelectrons up to 10 keV can be analyzed [1]. Since then, the system has been opened to industrial researchers and has served them as a powerful tool for directly exploring the electronic structure deep inside the material, such as electrode/dielectric interfaces buried in gate stack structures, which are not accessible by conventional XPS.

To achieve much larger probing depth than R4000, we developed a new HAXPES measurement system equipped with Focus HV-CSA 300/15 analyzer [2], by which the electron kinetic energy up to 15 keV can be analyzed. There are only a few literatures reporting the HAXPES spectra excited by photon energy more than 10 keV [2]. In the present paper, the details of the system and the HAXPES spectra excited by 14 keV with the energy resolution sufficient for practical analysis are reported.

2. Instrumentation

The system is illustrated in Figure 1. It consists of main and sub chambers. The four-axis (x, y, z, θ) sample manipulator, the electron analyzer, the neutralizer (PHI 04-091), and the electron gun (RDEC RDA-003G) are installed in the main chamber. The incident X-ray is introduced from the beryllium window (~ 100 nm) attached at the front of the main chamber. A large-sized sample holder ($78 \text{ mm} \times 28 \text{ mm} \times 12 \text{ mm}$) has adopted to load large number of samples at once (Figure 1(b)). From a large quick access window, the samples on the sample holder are loaded to the sub chamber and are transferred to the main chamber for the measurement. Three CCD cameras are attached for monitoring the samples.



The HV-CSA 300/15 analyzer consists of a cylindrical sector field analyzer, a pre-retarding lens system, and a 2-D event-counting detector equipped with a multi-channel plate (MCP), a phosphor screen, and a CMOS camera. The entrance slit of the analyzer has a rectangular shape with the three selectable sizes in the energy dispersive direction (4.5 mm, 1.5 mm, and 0.5 mm) and the fixed size (12 mm) in the non-dispersive direction. The lens mode can be selected from the magnification lists from 3 to 60, stepwise. The pass energies are continuously changeable from 1 to 500 eV. The HV-CSA has the advantage of increasing luminosity by the second order focusing property along the dispersive direction [2]. In addition, it has much less volume and weight than the other commercial hemispherical HAXPES analyzers.

The manipulator and the base frame can be controlled by spec programs of Scientific Certified Software through the pulse step motors. The analyzer is controlled by the genuine software ProCSA supplied by Focus, which can act as a TCP server for the external control by other systems. Using this function, several scan commands of spec were developed for the sample alignment easily.

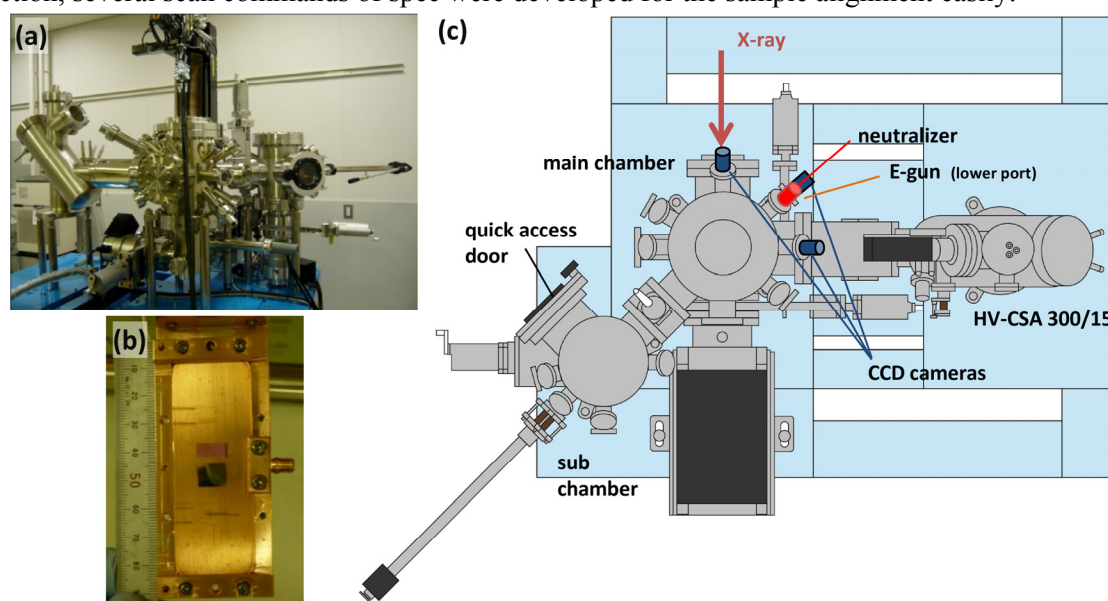


Figure 1. The HAXPES measurement system with Focus HV-CSA 300/15 analyzer up to 15 keV developed in this study. (a) Photograph of the system. (b) Sample holder. (c) Illustration of overall system from top view.

3. Experimental

The experiments were performed at the undulator beamlines, BL46XU and BL33XU, of SPring-8.

In BL46XU [1], the white light from the undulator is monochromatized by a Si double crystal monochromator (DCM). The X-ray beam was horizontally focused by Rh-coated 700-mm-long double bend mirrors with their incident angles set to 3.15 mrad. The size of the front-end slit was set to 0.7 mm (horizontal) \times 0.7 mm (vertical), and the other slits were set wide enough to avoid cutting the X-ray beam. The beam size at the sample was ~ 0.25 mm (h) \times ~ 0.5 mm (v).

In BL33XU [3], the white light is monochromatized by a Si channel-cut monochromator (CCM), and was horizontally and vertically focused by Rh-coated 1000-mm-long double upstream mirrors (M1, M2) and 700-mm-long double downstream mirrors (M3, M4), respectively. The incidence angles of the mirrors are set to 1.5 mrad for M1, M2 and 3.5 mrad for M3, M4. The size of the front-end slit was set to 0.5 mm (h) \times 0.5 mm (v), and the other slits are set so that the beam size at the sample was shaped into ~ 0.8 mm (h) \times ~ 0.15 mm (v).

In the both beamlines, Si(111) and Si(333) reflections were used to obtain monochromatized X-ray of 14 keV for the excitation of photoelectrons. The voltages for screen and MCP of the analyzer were set to 4500 V and 2600 V, respectively. The base pressure of the main chamber was $\sim 2 \times 10^{-8}$ Pa.

4. Results and Discussion

Figure 2 shows the Si 1s spectra of Si(100) substrate excited by 14 keV at different analyzer slit sizes, pass energies, and Si reflection plane for the monochromator. The peak widths by means of full width at half maximum (FWHM) are indicated in the inset. The peak width of Si 1s excited by X-ray of Si(333) DCM is considerably narrower than that of Si(111) DCM, indicating the difference in the X-ray energy resolution between the two reflection planes (theoretical energy resolution, $\Delta E/E$, for Si(111) and Si(333) are 1.1×10^{-4} and 8.5×10^{-6} , respectively [4]). The Si 1s peak width becomes smaller as the slit width gets narrower, indicating the energy resolution of the analyzer increases by narrowing down the slit width. The width is narrowest (0.95 eV in FWHM) at the slit size of 0.5 mm \times 12 mm and the pass energy of 50 eV, which is comparable to the results measured by R4000 with 8 keV X-ray (0.87 eV, not shown in this report).

Figure 3 shows the Si 1s spectra of 60 nm SiO₂ thin film formed on Si(111) substrate by thermal oxidation measured with 14 keV X-ray at different monochromator reflection planes, slit sizes, and take-off angles (TOAs). The Si 1s peak from the bulk-Si under the 60 nm-thick SiO₂ layer overlaps with the Si-oxide component in the spectrum with X-ray monochromatized by Si(111) DCM, while the bulk peak is clearly distinguished at ~ 12173 eV and well separated from the oxide component in that with X-ray monochromatized by Si(333) DCM. Thus the usage of Si(333) DCM reflection for 14 keV X-ray not only realizes the much deep probing depth, but also increases the energy resolution of X-ray and thus the total energy resolution of the measurement. At TOA = 30°, the peak of the bulk-Si is not clearly distinguished, since the probing depth at TOA = 30° is about a half of that at TOA = 80°.

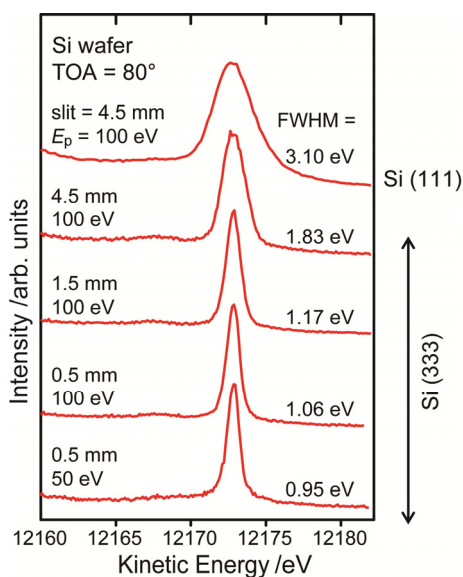


Figure 2. Si 1s spectra of Si wafer taken at $h\nu = 14$ keV as a function of the reflection planes of monochromator, analyzer slit widths, and pass energies.

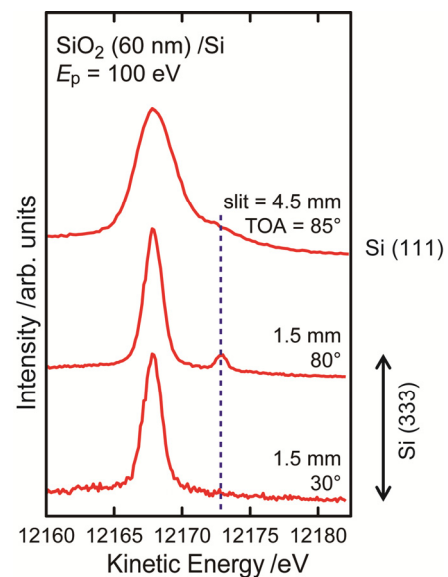


Figure 3. Si 1s spectra of SiO₂ (60 nm) / Si at $h\nu = 14$ keV as a function of the reflection planes of monochromator, analyzer slit widths, and TOAs.

The HAXPES spectra of 100 nm Au film sputtered on Si substrate by $h\nu = 14$ keV are shown in Figure 4. Unlike the conventional XPS, the relative intensity of Au 4f peaks are significantly low compared to Au 5s and 5p peaks, because the photoionization cross-section for the state with higher angular momentum quantum number decreases much faster than those with lower one as the excitation energy increases. The doublet peaks of Au 4f are well resolved, as shown in Figures 4 (a) and (b), where the peaks become much sharper as the slit width becomes narrower. Rubio-Zuazo *et al.*, reported the HAXPES spectra of Au (21 nm) on Cu polycrystal with $h\nu = 15$ keV, while 4f peak are not well resolved in their data, due to the worse total resolution by Si(111) DCM reflection [2]. As

shown in the Figure 4(c), one can see the Fermi edge and detailed valence band structures clearly in the spectrum. The total energy resolution estimated by fitting the Fermi-Dirac distribution function (the solid line in the figure) to the experimental curve is 0.50 eV.

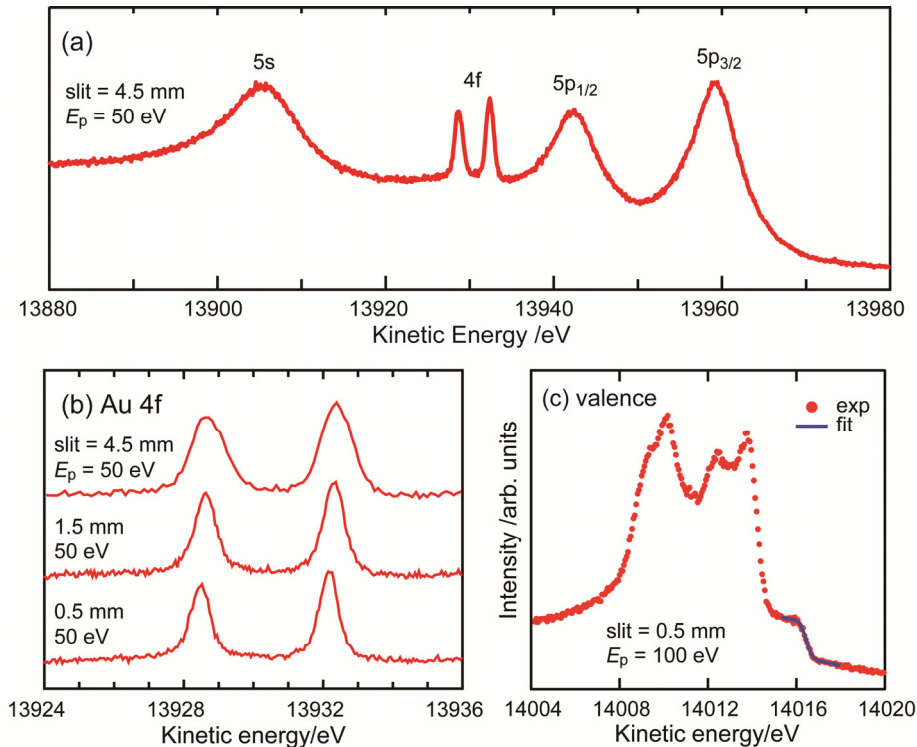


Figure 4. The HAXPES spectra of Au (100 nm) / Si taken at $h\nu = 14$ keV. (a) Survey spectrum from Au 5s to 5p regions. (b) Au 4f region. (c) Valence band spectrum. Experimental spectrum (filled red circles) is fitted with the Fermi-Dirac distribution function (solid blue line).

5. Conclusion

The HAXPES measurement system equipped with Focus HV-CSA analyzer with the electron kinetic energy up to 15 keV has been developed. With the X-ray monochromatized by Si(333) reflection and the proper setup of the analyzer, the energy resolution sufficient for the chemical state analysis has been achieved. Furthermore, the large probing depth of the system has been confirmed.

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