



Angular distributions of photoemission in hard X-ray photoelectron spectroscopy using linearly polarized light



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ABSTRACT

Characterizing the angular distributions of photoemission is important for evaluating the elemental composition of materials by hard X-ray photoelectron spectroscopy (HAXPES; HX-PES). These distributions cannot be explained by dipole approximation, and their parameters have been theoretically derived using non-dipole approximation. In this study, the angular distributions of photoelectrons emitted from 3s, 4s, 4p, 4d, and 4f states, observed directly using the HAXPES analyzer with a wide angle objective lens, were investigated by irradiating 8 keV X-rays onto a platinum (Pt) surface. In the 4d and 4f states, the obtained distributions were asymmetric relative to the X-ray polarization vector. This asymmetry was consistent with theoretical results using the non-dipole approximation. Thus, the angular distributions of photoemission predicted by non-dipole approximation were experimentally confirmed at various energy levels of Pt.

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1. Introduction

X-ray photoelectron spectroscopy is an extensively used technique in surface science research. Recently, hard X-ray photoelectron spectroscopy (HAXPES; HX-PES) has become one of the most powerful techniques for investigating bulk electronic and chemical properties of solids [1–9]. High-energy photoelectrons emitted by hard X-rays possess a long inelastic mean free path, leading to a deeper detection limit [10,11]. Although researchers have been especially interested in electronic and chemical properties of materials, elemental compositions are increasingly being sought for further material evaluations, using photoelectron intensities.

The intensities of photoelectrons emitted from amorphous samples with a uniform elemental composition are typically estimated from the photoionization cross section, angular distribution, and inelastic mean free path of the photoelectrons. The photoelectron angular distribution of free atoms and molecules irradiated by a polarized excitation source is calculated by dipole approximation [12]:

$$1 \propto \frac{\sigma}{4\pi} \left[1 + \frac{\beta}{2}(3 \cos^2 \theta - 1) \right] \quad (1)$$

where σ is the total photoionization cross section, β is a dipole asymmetry parameter, and θ is the angle between the X-ray and photoelectron paths. HAXPES generally requires high flux and high-energy-resolution photon beams in the 6–15 keV energy range, generated by third-generation synchrotron sources. However, it is reported that the angular distributions of photoemission by the hard X-rays cannot be expressed by the dipole approximation, of which experiments were performed in gaseous phase such as argon and krypton [13,14]. Subsequent theoretical studies have shown that the distributions may be fitted to a non-dipole approximation [15–17]. Hemmers et al. [18] developed an experimental apparatus dedicated to measurements of the dipole angular-distribution parameter and the first-order non-dipole parameters, and their combination, and reviewed non-dipole effects in soft X-ray photoemission [19]. Jackson et al. [20] proposed a method for measuring the non-dipole parameter based on condensed thin films, though the angular distributions are not observed directly. Accounting for non-dipole transitions, the angular distribution is written as follows [21–23]:

$$1 \propto \frac{\sigma}{4\pi} \left[1 + \frac{\beta}{2}(3 \cos^2 \theta - 1) + (\delta + \gamma \cos^2 \theta) \sin \theta \cos \varphi \right] \quad (2)$$

where γ and δ are angular parameters considering electric dipole–quadrupole and electric dipole–magnetic dipole contributions, respectively, to the photoionization process. In this approximation, angular distributions are tilted from the polarization vector toward the direction of the incident X-ray. This implies

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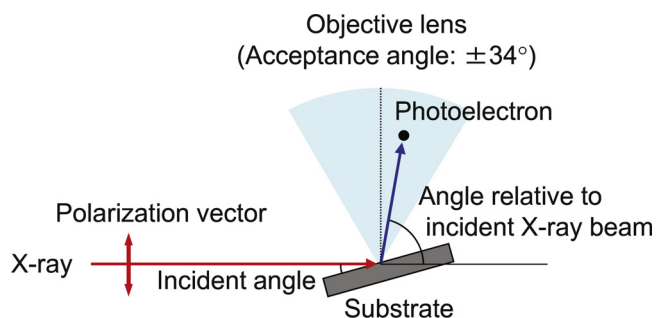


Fig. 1. Angles and directions of the incident X-ray beam and its polarization vector (red arrows), the sample (gray block), and the objective lens (observation range shown in light blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

that photoelectron intensities can change in the direction incident to the electron analyzer. In other words, angular distributions should be considered when estimating elemental composition from photoelectron intensities.

In this study, we investigate angular distributions of photoelectrons, by direct detection using the HAXPES analyzer with a wide angle objective lens, emitted from a platinum (Pt) surface by linearly polarized X-rays at a typical HAXPES energy, namely, 8 keV.

2. Experimental

The experiments were performed at the BL47XU beamline at the SPring-8 facility. The HAXPES apparatus is positioned in the beamline, and HAXPES spectra of solid surfaces are obtained by hard X-ray irradiation. The setup is detailed elsewhere [2,24].

To reduce their bandwidths (BW), X-rays are monochromatized by a Si(111) double-crystal beamline monochromator, followed by a Si(111) channel-cut post-monochromator. Finally, photon energies of 8 keV are obtained by the 444 Bragg reflection with intrinsic bandwidths of 38 meV. The available photon flux is 2.8×10^{11} photons/s/0.0005% BW, which is achieved by a mirror-focused beam of size $30 \mu\text{m}$ (horizontal, H) \times $40 \mu\text{m}$ (vertical, V). The stability of the electronics and power supplies is evaluated by measurements of Au 4f spectra over a 10-day period, recorded by a hemispherical electron energy analyzer (R-4000, VG-Scienta Co.), and it is confirmed to be extremely high. The peak and integrated intensities shift within ± 5 meV and $\pm 1\%$, respectively. The total energy resolution for typical parameters (pass energy = 200 eV; curved analyzer slit width = 0.5 mm), measured by the Fermi edge of Au at 8 keV photon energy, is estimated as 228 meV.

Since a two-dimensional detection system is built into the analyzer, we can resolve spectra along the lateral direction parallel to the entrance slit or in the angle of emission along the same direction. An electrostatic lens with a wide acceptance angle is installed in front of the analyzer. Although the designed acceptance angle of the first stage is $\pm 45^\circ$, when combined with the analyzer, it reduces to approximately $\pm 34^\circ$ because of the limitation imposed by the final acceptance angle of the R-4000 analyzer. The angular resolution has been estimated to be 1.32° .

The lens axis of the analyzer is placed perpendicular to the incident X-ray beam and parallel to the polarization vector. The incidence angle relative to the sample surface is set to 5° , as shown in Fig. 1. Since the irradiated surface is a metal (unless treated by processes such as vacuum heating), the test sample was Pt foil (thickness $100 \mu\text{m}$, Nilaco Co.) of which surface was amorphous because neither a spot nor a ring was observed by low energy electron diffraction (LEED). The pressure in the analysis chamber is less than 1×10^{-6} Pa. The energy of the incident X-ray is 7940 eV.

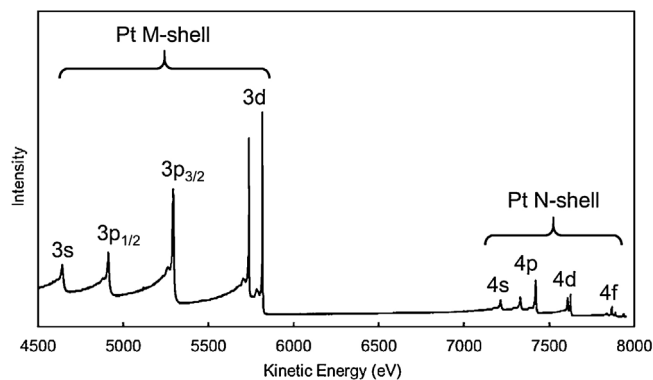


Fig. 2. HAXPES spectrum of Pt foil obtained by irradiation of 8 keV X-rays.

3. Results and discussion

A HAXPES spectrum of the Pt foil irradiated by 8 keV X-ray is shown in Fig. 2. The horizontal and vertical scales indicate the kinetic energy and intensity, respectively, of the emitted photoelectrons. Peaks in the 4500–6000 eV range are assigned to Pt M-shell states, while those in the 7000–8000 eV range are assigned to Pt N-shell states. Peaks attributable to carbon (7655 eV) and oxygen (7408 eV) are absent in Fig. 2, suggesting that neither carbon nor metal oxide exists within the Pt foil at the detection depth.

Fig. 3 plots angular distributions of the intensities of photoelectrons emitted from 3s and 4s states. The angular range (60 – 120°) is relative to the incident X-ray beam, and it is limited by the acceptance angle of the analyzer lens. The photoelectron intensities are determined as the area under the peaks in Fig. 2, and the backgrounds were subtracted by the Shirley method [25]. The absence of a local maximum in Fig. 3 indicates that no photoelectron diffraction occurs in the sample. Therefore, the sample is amorphous or polycrystalline, at least within the detection depth on the sample surface. The change in direction of the emitted photoelectrons, known as refraction through the solid–vacuum interface [26], is presumed small, because the momentum change causing the direction change (refraction) is relatively small in the direction close to the normal to the sample surface, especially at high photoelectron energies. Both distributions in Fig. 3 are maximized at 90° , are very similar in magnitude, and almost symmetric relative to the X-ray polarization vector. The slight difference between the

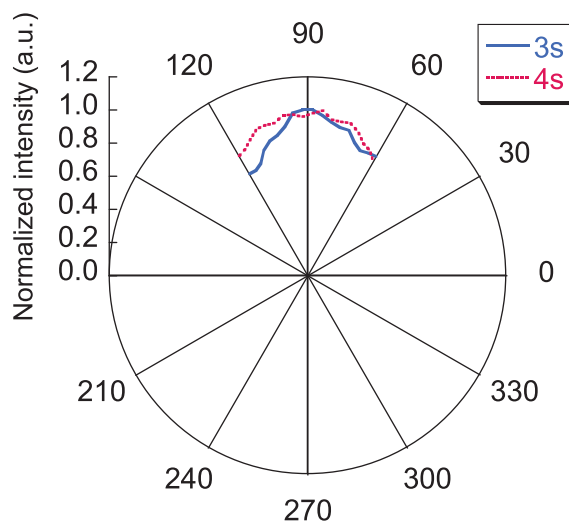


Fig. 3. Angular distribution of photoelectrons emitted from Pt in the 3s and 4s states, irradiated by 8 keV X-rays.

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