Photoelectron structure factor and diffraction spectroscopy

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ABSTRACT

The information obtained by all-direction-resolved photoelectron spectroscopy for valence band and core levels are described. By measuring two-dimensional photoelectron intensity angular distribution (PIAD) from valence band, the iso-energy cross section of valence band, *e.g.*, the Fermi surface can be observed. In the case of linearly polarized-light excitation, the symmetry relation in the photoelectron excitation process is also displayed as "angular distribution from atomic orbital", which is used to distinguish the atomic orbitals constituting the energy band. Another important effect in angular distribution is the "photoelectron structure factor (PSF)", which originates from the interference among photoelectron waves from individual atoms. The bonding character of the energy band can be clarified from the intensity inequivalency between Brillouin zones determined by PSF. On the other hand, the photoelectron from a localized core level is an excellent probe for element-specific atomic structure analysis. Photoelectron diffraction provides information on the surrounding atomic configuration, which is recorded as forward focusing peaks at local interatomic directions and diffraction patterns in PIAD. By combining this diffraction technique with core level spectroscopy – we call it diffraction spectroscopy, one can get access to each atomic site structure and have their electronic property information individually. Direct three-dimensional atomic structure visualization and site specific electronic property analysis methods are reviewed.

1. Introduction

Photoelectron spectroscopy is a powerful technique for the investigation of both electronic and atomic structure of solids and surfaces. Photoelectron energy distribution curves for valence band and core levels reflect density of states and compositions, respectively. Behavior of valence electrons and interference of photoelectrons are projected in momentum space as photoelectron angular distribution patterns. Based on the energy and momentum conservation principles in the photoemission process, all-direction-resolved photoelectron spectroscopy provides a rich variety of information on the electronic and atomic structure of solids.

The electronic properties and chemical reactivity of materials are closely related to the behavior of electrons at vicinity of Fermi level. Angle-resolved photoelectron spectroscopy for valence band dispersion mapping is a powerful technique to study such electrons. Two-dimensional photoelectron intensity angular distribution (PIAD) corresponds to the iso-energy cross section of valence

band. Three-dimensional energy band dispersion (k_x, k_y, binding energy) [1] and Fermi surface (k_x, k_y, k_z) [2] are obtained by measuring a series of PIAD as function of the binding energy and excitation photon energy, respectively.

In the case of linearly polarized-light excitation, the symmetry relation in the photoelectron excitation process is also displayed as "angular distribution from atomic orbital (ADAO)" [3], which is used to distinguish the atomic orbitals constituting the energy band. Another important effect in angular distribution is the "photoelectron structure factor (PSF)" [3–5], which originates from the interference among photoelectron waves from individual atoms. The bonding character of the energy band can be clarified from the intensity inequivalency between Brillouin zones determined by PSF.

On the other hand, the photoelectron from a localized core level is an excellent element-specific probe for atomic structure analysis. Photoelectron diffraction provides information on the surrounding atomic configuration, which is recorded as forward focusing peaks (FFPs) at local interatomic directions [6–8] and diffraction rings around them in PIAD. Furthermore, FFPs were found to show rotational shifts when excited by circularly polarized light. FFP shift has been shown to be inversely proportional to the distance between the emitter and scatterer atoms both
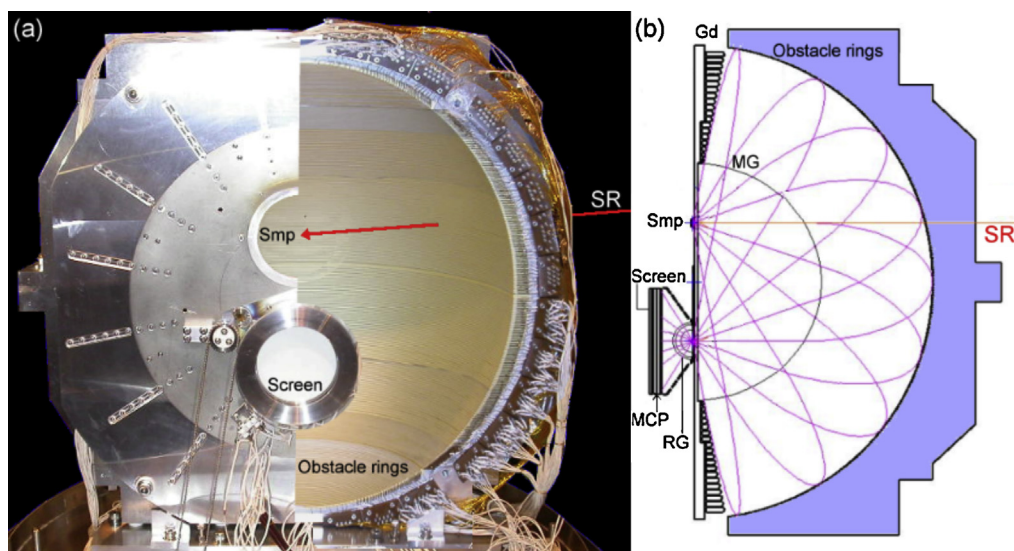
Fig. 1. (a) Photograph and (b) schematic diagram of display-type analyzer installed at BL25SU, SPring-8.

experimentally [9] and theoretically [10]. This is the basis for the stereo photography of the atomic arrangements [11–13].

Moreover, we have been developing a new approach for investigating the properties of specific atomic site non-destructively. Since PIAD differs by different surrounding atomic arrangement, emitter atom sites can be specified by their characteristic diffraction patterns. By combining this diffraction technique with core level spectroscopy – we call it *diffraction spectroscopy*, one can get access to each atomic site structure and have their electronic property information individually [14]. We have applied this method to study various subsurface structures and electronic properties [14–16].

In this paper, the information obtained by all-direction-resolved photoelectron spectroscopy for valence band and core levels are described. It is noteworthy that the quantum phenomena in initial states (band dispersion) and final states (photoelectron diffraction) are both well observed in the valence PIAD at high kinetic energy. The circular dichroism of photoelectron FFP rotation around the incident-light axis reflects the orbital angular momentum of excited core level [11]. But, these rotations are also found in the case of the valence band photoelectrons with high kinetic energy [17]. The orbital angular momentum quantum number of valence electron for specific site can be deduced from the FFP rotation [17,18].

2. Experimental details

One efficient approach to measure photoelectron and Auger electron patterns at specific kinetic energy are by using a display-type analyzer. For example, a two-dimensional display-type spherical mirror analyzer (DIANA) [19] shown in Fig. 1 enables 1π-steradian ($\pm60°$) PIAD direct observation without changing the angles of incident light and the sample orientation. It consists of a hemispherical main grid (MG), outer sphere with obstacle rings (OR) and guard rings (Gd). The potential $V(r)$ of obstacle rings and guard rings are biased according to their distance r from the center of the analyzer by the formulae,

$$V(r) = -2E_0 \left(1 - \frac{a}{r}\right)$$

where E_0 is the kinetic energy of electron to be analyzed and a is the radius of the main grid. The electrostatic field in the space surrounded by the main grid, obstacle rings and guard rings is thus

made spherically symmetric with respect to the center of analyzer. Synchrotron radiation light for excitation (SR) is introduced through a hole. In this case of DIANA installed at BL25SU in SPring-8 [20], light is incident from the direction 45° inclined from the center of the analyzer. The orbits of the emitted electrons from the sample are subjected to this field after passing through the main grid, and their loci are ellipsoids obeying the Kepler's law. Their trajectories inside the main grid are straight lines. The electrons converge exactly to the exit aperture, which is located at the symmetric position of sample (Smp) with respect to the center of analyzer.

The obstacle rings work as a "low-pass filter" in energy analysis. An electron having slightly higher energy than E_0 travels on slightly outside locus, collides with the obstacle rings and is removed. On the other hand, the retarding grids (RG) works as a "high-pass filter", which retards the electrons that have lower kinetic energies than the applied potential, E_{RG}. The electrons, having passed through the retarding grids, are amplified by a pair of micro channel plates (MCP), and are converted to light pulses by a phosphorous screen, which are detected from outside the vacuum chamber by a CCD camera. The acceptance cone angle covered by the MCP is $\pm60°$. If the surface normal direction was set along the photon incident axis, the emission angle (θ) dependence from $45\pm60°$ relative to the surface normal was measured simultaneously. By scanning the sample azimuth over 360°, 2π-steradian photoelectron diffraction data were collected [21,22].

Fig. 2(a) shows a series of Cu LMM Auger electron intensity angular distribution (AIAD) projected on the fluorescent screen. Photon energy was set to 931 eV. The potential $V(r)$ was tuned to detect electrons with kinetic energy of 913.5 eV. The energy window ($\Delta E \equiv E_0 - E_{RG}$) was set to 10 eV. Soft X-ray was incident from surface normal direction. Sample orientation was varied from 0° to 360° by 9° step. Dwell time was 5 s for each AIAD acquisition. Total acquisition time was about 5 min. They are assembled to one 2π-steradian AIAD shown in Fig. 2(b). However, this pattern contains artifacts due to detection inhomogeneity, such as dark spot near the center, which can be removed by the following procedure. Fig. 2(c) is a polar angle dependence pattern obtained by averaging AIAD intensity shown in Fig. 2(a) along azimuthal angle. Inhomogeneous detection efficiency distribution was obtained by simply averaging all the measured data shown in Fig. 2(a). Position of Auger electron diffraction pattern on the screen varies as the sample orientation changes, but the position of artifact pattern due to