Stereo atomscope and diffraction spectroscopy—Atomic site specific property analysis

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Direct three-dimensional atomic structure analysis by stereo atomscope, valence-band angular momentum analysis by circularly polarized photoelectron diffraction, and atomic-layer-resolved magnetic structure analysis by diffraction spectroscopy are reviewed. The circular dichroism of photoelectron forward focusing peak rotation around the incident-light axis reflects the orbital angular momentum of excited core level and is inversely proportional to the distance between the emitter and scatterer atoms. This is the basis for the stereo photograph of the atomic arrangements. Furthermore, these rotations are also found in the case of the valence band photoelectrons. The rotation corresponds to the orbital angular momentum quantum number of valence band. Simultaneously, the photoelectron structure factor, that corresponds to the interference of photoelectron waves from atomic orbitals within a unit cell, was observed. The origin of the dual behavior that appeared in the observation of local angular momentum from a delocalized valence band is discussed. Lastly, local electronic and magnetic structure information has been obtained by diffraction spectroscopy. X-ray absorption and magnetic circular dichroism spectra from different atomic layers of the Ni thin film were disentangled by use of Auger electron diffraction. Surface and interior core-level shifts and magnetic moments are determined for each atomic layer individually.

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1. Introduction

We analyze the intensity of electrons liberated from solids by photoexcitation as functions of kinetic energy and momentum to obtain information on density of states, band dispersions, chemical compositions, atomic arrangements and so on. Now, photoelectron spectroscopy measurements at extremely high energy resolution become possible thanks to the continued technological innovations. However, with exception of Fermiology, less attention has been paid to the acquisition of photoelectron intensity angular distribution (PIAD) in a wide solid angle. Another important physical quantity, i.e. angular momentum of photoelectron, can be accessible only by the analysis of PIAD. This quantity is directly related to the information on atomic orbitals. Indeed, various exotic electronic properties of solids result from the interplay of electrons in atomic orbitals.

In this review, we describe our new approaches of atomic level property analysis by two-dimensional photoelectron spectroscopy and diffraction measurements. First, we briefly introduce a display-type analyzer (DIANA) [1–3]. The key point in the measurement of photoelectron angular momentum is to fix the relation between sample orientation and electric vector of incident photon during the measurement of PIAD. DIANA is suitable for this purpose because PIAD can be measured at a time without changing the directions of the sample and the incident light.

In the following section, the principle and the applications of Stereo Atomscope are presented [4]. The photoelectron from a localized core level is an excellent probe for element-specific atomic structure analysis [5–9]. The configuration of surrounding atoms are recorded as forward focusing peaks (FFPs) at local interatomic directions and diffraction patterns in PIAD [10–12]. Furthermore, FFPs were found to show rotational shifts when excited by circularly polarized light [13]. FFP shift has been shown to be inversely proportional to the distance between the emitter and scatterer atoms both experimentally [13,14] and theoretically [15]. Taking advantage of this circular dichroism, a stereo atomscope was realized [4,16–20].

Then, we turn our attention to the valence band excitation. Three-dimensional Fermi surfaces and band dispersions have been visualized by two-dimensional photoelectron spectroscopy with DIANA and vacuum ultraviolet (VUV) light [21–23]. Surprisingly, FFPs also appear in the PIAD at high kinetic energy from well delocalized valence band [24–30]. However, the mechanism of FFP formation in the PIAD from valence band has remained unclear.

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We challenged this issue by measuring the circular dichroism angular distribution (CDAD) of graphite for each band (2p_x, 2p_y, 2s) [29]. The interference of photoelectron waves excited from several atomic orbitals within the same unit cell produces a specific pattern in a reciprocal space, which is called the photoelectron structure factor (PSF) [21,31–33]. At the same time, we observed significant FFP rotational shifts around incident photon axis as in the case of core photoelectrons. Moreover, the rotational shift was found to correlate with the angular momentum quantum number of valence band. This dual behavior that appeared in the observation of local angular momentum from a delocalized valence band is discussed in conjunction with the dispersion and spatial origin of the electron.

Photoelectron and Auger electron diffractions are the strong tools for atomic structure analysis. Occupied electronic states can be accessed by photoelectron spectroscopy, X-ray absorption spectroscopy and X-ray magnetic circular dichroism measurements by Auger electron yield detection, on the other hand, are powerful analysis tools for the conduction electronic and magnetic structures. However, all the information from atoms within the electron mean-free-path range is averaged into the obtained spectra.

As the third topic, we introduce a new method of disentangling spectra from different atomic layers by use of Auger electron diffraction. Taking advantage of the FFP as an excellent element- and site-selective probe, diffraction spectroscopy enables direct access to the electronic and magnetic structures of subsurface atoms. We have applied this method to studying the electronic and magnetic structures of Ni thin film at atomic level [34].

We note here that another complimentary method, photoelectron holography, has been introduced in detail as a separate review in this volume.

### 2. Display-type analyzer

PIAD from sample at specific kinetic energy is most efficiently measured by a two-dimensional display-type spherical mirror analyzer (DIANA) [1–3]. PIADs are projected on a fluorescent screen with the emission angle preserved. Thus, the emitted direction of the photoelectrons can be deduced directly from the position of the PIAD pattern on the screen. Fig. 1 shows a schematic view of the DIANA [35] recently installed at the VUV beamline BL-7 of Ritsumenkan SR Center, Japan. It consists of a hemispherical main grid (G), outer sphere (OS) with 151 obstacle ring electrodes (OR), and 5 guard rings (GR). The potential V(r) of ORS and GRs are biased according to their radii r from the center of the analyzer by the formula,

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

where \(E_0\) is the pass energy and \(a\) is the radius of the main grid G. The main grid \(G (a = 64 \text{ mm})\) for the high energy resolution version was fabricated using a #50 line/in. woven mesh with the wire diameter of 0.05 mm. On the other hand, the main grid \(G (a = 150 \text{ mm})\) for a stereo atomscope [4], was fabricated using 0.4 mm thick titanium hemisphere to prevent distortion from an exact hemisphere by its own weight. Holes 0.5 mm diameter in size were made by electron beam processing on all over the hemisphere. The electrostatic field in the space surrounded by the electrodes G, ORS and GRs is thus made spherically symmetric with respect to the center of analyzer.

Excitation light is introduced through a hole. The orbits of the emitted electrons from the sample are subjected to this field after passing through G, and their loci are ellipsoids obeying the Kepler’s law [36]. Their trajectories inside G are straight lines. The electrons converge exactly at the exit aperture S, which is located at the symmetric position of sample S with respect to the center of analyzer. Analyzer, manipulator and sample holder were demagnetized. To reduce a residual magnetic field and achieve higher performance, two-fold \(\mu\)-metal shields were mounted inside the vacuum chamber and outside the analyzer. Residual magnetic field inside the analyzer is less than around 1 mGauss.

The ORS works as a “low-pass filter” in energy analysis. An electron having slightly higher energy than the pass energy \(E_0\) travels on slightly outside locus, collides with the electrodes ORS 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. The energy resolution \((\Delta E / E_0)\) of the present analyzer has been estimated to be about 0.3% of the pass energy. The angular resolution was \(\Delta 1^\circ\).

The electrons, having passed through the retarding grids, are amplified by a pair of microchannel plates (MCP), and are converted to light pulses by a phosphorous screen (P), which are detected from outside the vacuum chamber by a CCD camera. The acceptance cone covered by the MCP is \(\pm 60^\circ\) or \(1\pi\) steradian. The two-dimensional angular distribution on the screen is the same as the original one in front of the sample. Widely used angle-resolved electron analyzer, concentric hemispherical analyzer (CHA) for instance has one order higher energy and angular resolutions. However it requires a lot of time to take full-solid-angle angular distribution of emitted electron intensity because the acceptance angle of CHA is narrow, about \(7^\circ \times 1^\circ\), which corresponds to about 0.001 \(\pi\) steradian.

DIANA equipped with microwave-excited He light source [22] or installed at VUV beamline [35] are used for the valence band study. PIAD measurements are done at normal incidence geometry. Since sample, analyzer, and incident light electric vector are fixed, band dispersion and transition matrix element effect can be studied simultaneously.

DIANA for a stereo atomscope [3], is installed at the circularly-polarized soft X-ray solid-spectroscopy beamline BL25SU at SPring-8, Japan [37]. Helicity \(\sigma_+\) of monochromatized circularly polarized soft X-ray was reversed by switching the path of storage ring electron in twin helical undulators at 0.1 Hz [38]. In this case, light was incident from the direction 45° inclined from the center of the analyzer. By using this DIANA, PIAD can be obtained directly on the screen.

### 3. Stereo atomscope

The circular dichroism in photoelectron intensity is generally regarded as a useful probe for the investigation of magnetism.
Fig. 2. (a) Parallax in stereo viewing. (b) Schematic drawing of propagation of photoelectron wave excited by circularly polarized light.

But it is much more universal phenomena even for nonchiral and non-magnetic materials [13,14]. When the kinetic energy of a photoelectron is higher than several hundred electron volt, a strong FFP appears along the direction connecting the emitter and the scatterer [10–12]. The positions of FFPs in the two-dimensional PIAD excited by the circularly polarized light rotate in the same direction as the rotation of the electric vector of the incident light. FFP shift has been shown to be inversely proportional to the distance between the emitter and scatterer atoms [13–15].

Stereo viewing is achieved when object is seen by two eyes. As shown in Fig. 2(a), parallax becomes larger for the object located at smaller distance from the viewer. Taking advantage of these FFP parallax shifts, a stereo atomscope for atomic arrangements was realized [4,18]. Two photographs of an atomic

Fig. 3. (a and b) Stereo photograph of W crystal. (c) Three-dimensional configuration of atoms imaged by stereo photograph of (a) and (b). (d) Structure of W crystal.

Fig. 4. Cu3p PIAD from Cu(001) surface. (a) PIAD taken with $\sigma_-$ and $\sigma_+$ circularly polarized light. Dots indicate the position of FFPs. (b) Schematic diagram of the atoms around the emitter projected to the screen. Circles indicate polar angle directions of 15°, 30° and 45°. (c) Crystal structure and incident light.
arrangement with parallax shifts can be obtained by using a DIANA.

For example, the PIAD of W 4f photoelectrons from the W[110] surface at a kinetic energy of 800 eV is shown in Fig. 3(a) and (b)[4]. These patterns were observed on the analyzer’s flat screen. Fig. 3(a) and (b) was taken with cw and ccw circularly polarized light, respectively. The center of the figure nearly corresponds to the surface normal direction, which is the [110] axis, and the horizontal direction is [001]. The ccw and cw incident excitation light is inclined 45° to the surface normal, which is the [011] direction, as shown in Fig. 3(d). We can see five FFPs, such as A, B, C, C', and C'', in the directions shown in Fig. 3(c), which are the direction of the nearest-neighbor atoms such as A, B, C', and C'', in Fig. 3(d) seen from the emitter. The positions of these FFPs in Fig. 3(a) and (b) are the same as the direction shown in Fig. 3(c), but their positions are slightly different from the directions shown in Fig. 3(c). The patterns obtained by clockwise and counterclockwise light are symmetric with respect to the central vertical line. For example, the [110] peak A is slightly off center to the right in (a) and left in (b), as shown by the dots in the figure. Consequently, if we view the cw circularly polarized-light, PIAD (Fig. 3(a)) with the left eye and the ccw pattern (Fig. 3(b)) with the right eye, we can produce an image of a three-dimensional arrangement of atoms in a W[110] crystal, as shown in Fig. 3(c). The A atom looks closer, and the B and C atoms look farther away, and the others look the farthest. Moreover, nearby atoms appear strongly while more distant atoms look faint just as in a real view. The elongation of atom A is due to the projection of the pattern onto a flat screen. Fig. 4 is another example of stereo photograph for Cu(0 0 1) surface. Cu atoms arranged in fcc crystal lattice can be imaged.

Recently, even real-time visualization has been achieved [20].

3.1. Principle

In the case of core-level excitation, interference between the photoelectron direct wave $\psi^0$ from emitter atom and the scattered wave $\psi_{\text{scat}}$ from atom nearby produce PIAD. PIAD is described by a square of the sum of $\psi_0$ and all the $\psi_{\text{scat}}$ from nearby atoms at $r_m$,

$$I(\theta, \phi) = |\psi^0|^2 + \sum_{n} |\psi_{\text{scat}}|^2. \tag{2}$$

$\theta$ is the polar angle relative to surface normal, $\phi$ is the azimuthal angle from $x$-axis in surface $xy$ plane. When the kinetic energy of a photoelectron is higher than several hundred electron volt, $|\psi_{\text{scat}}|^2$ and the interference terms form a strong FFP along photoelectron wave propagating direction.

The characteristic feature of the photoelectrons excited by circularly polarized light is that they have orbital angular momentum around the incident light. Here, we consider the photoelectrons from C 1s core state with the quantum number of the angular momentum $l_c = 0$ and its z-component $m_l = 0$. The quantum axis (z-axis) is the traveling direction of the incident circularly polarized light. A circularly polarized light $\sigma_\pm$ with the photon angular momentum $\pm 1$ (Fig. 5) excites the ground state with the magnetic quantum number $m_c$ to the final state with $m = m_c \pm 1$. In other words, the $\pm 1$ angular momentum is given to the photoelectron by circularly polarized light in photoexcitation process. The final state wave function outside the emitting atom is expressed as

$$\psi^0 \propto \frac{e^{ikr} Y_{lm}(\theta, \phi)}{r} \Theta_{lm}(\theta), \tag{3}$$

$\Theta_{lm}(\theta)$ is the polar angle part of the spherical harmonics. The phase of the wave is expressed as $\exp[ik(R_0 + m\phi)]$. The constant phase surface forms spiral as shown in Fig. 2(b).

The propagation direction of this final state wave function is perpendicular to the spiral wave front. As the result of the propagation direction shift, FFP appears at $\Delta_\phi$ off from the direction of scatterer atom. As depicted in Fig. 2(b), $\Delta_\phi$ is expressed by a simple formula [13]

$$\Delta_\phi = \tan^{-1} \frac{m}{kR \sin^2 \theta}, \tag{4}$$

where $m$ is the magnetic quantum number of photoelectron, $k$ is the wave number of photoelectron, $R$ is the interatomic distance between emitter and scatterer atoms, $\theta$ is the angle between the incident photon direction and the outgoing direction of the emitted photoelectrons. In general case, the effective magnetic quantum number $m^*(\theta)$ considering the contribution to the transition from different $m_c$ initial states weighted by the transition probability at $\theta$ is used [Fig. 6][39]. The effective magnetic quantum number $m^*(\theta)$ for $l = l + 1$ channel is as follows.

$$m^*(\theta) = \sum_{l=-m}^{m} \sum_{m_l} |c(l+1, m', l, m)|^2 \Theta_{l+1,m_l} \tag{5}$$

Interatomic distance between emitter and scatterer atoms can be deduced from the FFP shift by Eq. (4) using $m^*(\theta)$.

3.2. Experimental verifications

3.2.1. Si(001)

We measured 2π steradian (full hemisphere) Si 2p PIAD from Si(001) surface [40]. Fig. 7 is a schematic diagram of DIANA.
and measurement set-up. Sample was mounted on a five-axis manipulator. Light was incident from the surface normal direction. Photoelectrons emitted from the sample are energy-analyzed and PIAD is projected onto the fluorescent screen with the emission angle preserved. The emission angle (θₑₑ) dependence from 0° to 90° with respect to the surface normal was measured simultaneously. By scanning the sample azimuth for 360°, 2π steradian PIAD was obtained [41]. Total acquisition time for a pair of 2π steradian PIADs excited by σ⁺ and σ− helicity light was 2 h.

Fig. 8(a) shows a series of PIADs excited with σ⁺ and σ− helicity light together with circular dichroism patterns. Photoelectron kinetic energy was 600 eV. Azimuthal angle was varied from −5° to 365° at the interval of 5°. FFP in the [0 0 1] direction marked with dot matches with rotational axis. The other FFPs rotate around the Polaris-like [0 0 1] FFP. FFPs in the (0 1 1) and (1 1 1) directions indicated by open circles move from left to right as the sample rotates.

In the case of σ⁺ excitation, FFP rotational shifts in counterclockwise direction were observed, while in the case of σ− excitation, shifts were in clockwise direction. In the circular dichroism patterns shown in Fig. 8(b), such shifts appear as a pair of bright and dark patterns.

Fig. 9(a) and (b) is a pair of σ⁺-excited PIADs displayed in stereo projection. ‘Gaussian weight coefficients’ having a peak at the center of the screen were multiplied to 74 PIADs. Then the series of azimuthal angle scanned PIADs were summed at each angle [41]. No symmetry operation was applied. Four-fold rotational symmetry is seen due to superimpose of the diffraction patterns from two non-equivalent atom sites A (0 0 0) and B (1/4 1/4 1/4) shown in Fig. 10, which have 90° rotated two-fold atomic arrangement.

The center corresponds to surface normal [0 0 1] direction which is also the direction of the incident-light axis. Bright spots in the four directions (θ = 54.7°) correspond to the FFPs of the first nearest atoms in the (1 1 1) directions. Angle of rotational circular dichroism was ±2.5°. In between two (1 1 1) FFPs, the FFPs of the second nearest atoms in the (0 1 1) directions (θ = 45°, φ = ±45°, ±135°) appeared. Angle of rotational circular dichroism was ±1.8°. Finally, traces of (1 1 0) FFPs were observed at horizon (θ = 90°). Angle of rotational circular dichroism was ±0.9°. Parallax shift for nearest atom is larger compared to that of the second nearest atom.

From two PIADs, stereo photograph of Si atomic arrangement was obtained as shown in Fig. 11[40].

Note that the broad structure around (1 1 2) directions (θ = 35.3°) is split into two parts. The position of intensity maxima in the feature around (1 1 2) directions shows circular dichroism in opposite side. In order to clarify this reason, we examined diffraction pattern in more detail.

Two 2π steradian PIADs were summed and shown in Fig. 9(c). Diffraction rings [42] were investigated and their radii were determined from the systematic PIAD analysis of photoelectron kinetic energy dependence. Radii of the first order diffraction rings around [1 1 1], [1 1 0], and [0 0 1] FFPs were 38.0°, 24.0°, and 22.5°, respectively.

The first order diffraction rings around (1 1 1) directions overlaps with FFPs in (0 1 1) directions. They enhance circular dichroism intensity of (0 1 1) FFPs. On the other hand, the first order diffraction rings around (0 1 1) directions appears at about 6° off from FFPs in (1 1 2) and 10° off from FFPs in (1 1 1) directions. FFPs in (1 1 1) directions due to first nearest atoms appear strong compared to the (0 1 1) diffraction rings, however, those in (1 1 2) directions have comparable intensity with that of the (0 1 1) diffraction rings. Two split parts in the broad structure around (1 1 2) direction are due
Fig. 9. Stereo projection of 2π steradian Si 2p PIAD. (a–b) The case of excitation with \( \sigma^+ \) and \( \sigma^- \) helicity light, respectively. (c) Summation of two is shown. Dots and circles indicate forward focusing peaks and diffraction rings.

to the diffraction rings around \( \langle 011 \rangle \) directions and rotates in the same direction as \( \langle 011 \rangle \) FPP. Rotational shifts in \( \langle 112 \rangle \) directions were also expected. However the circular dichroism of diffraction rings were more pronounced in this case. FFPs in \( \langle 112 \rangle \) directions rotate little and rather enhance the circular dichroism of these diffraction patterns. This is the reason of the circular dichroism in opposite side.

Observed FFP rotational shift of 2.5° in the Si 2p PIAD was largest at the \( \langle 111 \rangle \) directions. However it was smaller than the expected value of 4.6° calculated from the corresponding Si—Si bond length of 2.351 Å. Si atoms occupy two sites, \( \lambda \) and \( \beta \), in a diamond structure lattice, as shown in Fig. 10. Si core-level PIAD is a superimpose of the contributions from both sites. Hence the FFP rotational shift at the \( \langle 111 \rangle \) directions is smaller than the value expected from the Si—Si bond length due to the scattering at two different bonding distance.

3.2.2. InP(0 0 1)

As seen in the case of Si, it is not a trivial issue to clarify whether the FFP rotational shift at \( \langle 111 \rangle \) directions is the superimpose of a local scattering events at two different sites or the result of multiple scattering events. We have chosen InP, a typical zinc blende structure crystal, for answering to this issue. Structure model of InP together with incident light is depicted in Fig. 12(a). One fourth of cube is removed to show the cross-section of \( \{110\} \) and \( \{1\bar{1}0\} \) planes. Two sites, i.e. \( \lambda (000) \) and \( \bar{\beta} (1/4\ 1/4\ 1/4) \), are occupied by In and P atoms, respectively. Note that the upper nearest P atom seen from an In emitter atom locates at the \( [1\bar{1}1] \) direction but not at \( [\bar{1}\ 1\ 1] \). Since photoelectron diffraction is element selective probe, we can identify FFP rotational shifts at \( [1\bar{1}1] \) and \( [\bar{1}\ 1\ 1] \) separately by measuring PIADs from In and P cores separately. We have measured 2π steradian In 3d PIADs from InP(0 0 1) surface [43].

Fig. 13(a) and (b) are the set of 2π steradian In 3d PIADs excited with \( \sigma^+ \) and \( \sigma^- \) helicity light, respectively. They are displayed in stereo projection. Fig. 13(c) is the circular dichroism pattern, i.e. difference of Fig. 13(a) and (b). Photoelectron kinetic energy was 800 eV. High symmetric directions and planes are indicated in Fig. 12(b). FFP in the \( [001] \) direction at the center of PIAD matches with incident-light axis.

Two intense peaks at the \( [111] \) and \( [\bar{1}\ 1\ 1] \) directions are the FFP created by the nearest P atoms. In the \( \langle 101 \rangle \) directions, four FFPs created by the nearest In atoms are observed. Four Kikuchi-pattern-like feature along the \( \{111\} \) planes are also observed which are absent in the Si 2p PIADs [40]. FFPs also appear at the \( [\bar{1}\ 1\ 1] \) and \( [1\bar{1}1] \) directions but less intense compared to those at the \( [111] \) and \( [\bar{1}\ 1\ 1] \) directions. This is due to a local \( T_d \) symmetry of the zinc blende structure. The distance to the scatterer atoms at the \( [\bar{1}\ 1\ 1] \) direction is three times larger than the distance at the \( [111] \) direction. Position of FFPs corresponding to the scatterer atoms within 4 nm distance are shown in Fig. 13(d).

Note that the FFPs shift to clockwise direction in the case of \( \sigma^- \) helicity light excited PIAD, while shift to counterclockwise direction in the case of \( \sigma^+ \) helicity light excited PIAD. Fig. 14 shows the azimuthal angle dependence of photoelectron intensity at the polar angle \( \theta_{\text{out}} \) of 54.7°. Cross-sectional intensity profiles of four \( [111] \) FFPs are indicated.

Fig. 10. Structure model of diamond lattice. Arrows indicate incident light. Two kinds of non-equivalent sites are labeled as \( \lambda \) and \( \beta \).

Fig. 11. Si 2p PIADs from a Si(001) surface excited with \( \sigma^+ \) and \( \sigma^- \) helicity light. Intense peak at the center corresponds to the forward focusing peak at the \( [111] \) direction.
There are two types of circular dichroism. One type is the rotational shift well described by the formula (4) [13]. Rotational shifts of the FFPs at [1 1 1] and [−1 −1 1] directions were large, while the FFPs at [−1 1 1] and [1 −1 1] directions were small. This is because the distance to the scatterer atoms at the [−1 1 1] direction is three times larger than the distance at the [1 1 1] direction.

Fig. 15 shows the In 3d PIADs from a InP(001) surface excited with σ_+ and σ_− helicity light. Intense peak at the center corresponds to the FFP and the [1 1 1] direction. In the case of σ_+ excitation, FFP shifts to right, while in the case of σ_− excitation, FFP shifts to left. When left and right patterns are seen by left and right eyes, respectively, stereo image of atomic arrangement in the [1 1 1] direction is formed. The nearest P atom at the [1 1 1] direction pops out followed by two In atoms at the {1 0 1} directions.

Another type is the intensity change. As discussed in the Si case, diffraction rings formed around FFP also show such rotational shift. The overlapping diffraction ring modifies the FFP intensity [40]. Three peak features appeared in between [1 1 1] and {1 1 1} FFPs are labeled α, β, and γ [44]. Similarly, those appeared in between {1 1 1} and [1 1 1] FFPs are labeled α′, β′, and γ′. Feature α is intense in the case of σ_+ excitation, while feature α′ is intense in the case of σ_− excitation.

Finally, we take our attention to the Kikuchi-band-like features along the {1 0 1} and {1 1 1} plane directions. Kikuchi-band-like features appears along the {1 0 1} plane directions in case of Si 2p PIAD [40]. Similar but weak features are also observed in the present InP case. On the contrary, Kikuchi-band-like features along the {1 1 1} plane directions appeared in the In 3d PIAD were absent in the Si 2p PIAD as shown in Fig. 9. It is rather similar to the fcc Cu [41] and Ni [34] cases where Kikuchi-band-like features appear along the {1 1 1} plane directions.

In the circular dichroism pattern shown in Fig. 13(c), the FFP rotational shifts appear as a pair of dark and bright features. Most distinct feature can be found at the [1 1 1] and [1 1 1] directions. Notice that the dark and bright features align along (1 1 1) and (−1 1 1) Kikuchi-band-like lines, but not along (1 0 1) lines. Clockwise side of the line is bright while counterclockwise side of the line is dark. This is attributed to the rotation of FFPs caused by farther In atoms within {1 1 1} and {1 1 1} planes and two peaks above it correspond to {1 0 1} FFPs.

Kikuchi patterns observed in the electron diffraction at high kinetic energies consist of a set of Kikuchi bands edged with Kikuchi lines on both sides. The mechanism responsible for the sharp edge regions in the Kikuchi bands involves Bragg reflection of electrons from a set of parallel planes. Width and profile of Kikuchi band are determined by a crystal lattice plane interval and electron kinetic energy as well as potentials of atoms. Kikuchi-band-like features are also observed in the PIADs at the kinetic energies around 1000 eV where the photoelectron mean free path is considerably long [45–50]. Omori et al. have measured the Ca 2p (1140 eV) and F (801 eV) PIADs from CaF_2 using Al Kα radiation and succeeded in deducing the three-dimensional crystal structure based on Kikuchi band analysis [46–48]. Similar investigations were reported for the case of Si [49,50]. On the contrary, application of such analysis was difficult in the case of InP along {1 0 1} plane directions, where contributions of FFPs are large. This is explained by the stronger scattering by the atomic potential of In (Z = 49) compared to those of Ca (Z = 20) and F (Z = 9) atoms. As a result, FFP of In atoms along {1 0 1} plane directions are much apparent compared to that of the Kikuchi band edge profile.

To summarize, the FFPs at [1 1 1] and [1 1 1] directions were intense, while the FFPs at [1 1 1] and [1 1 1] directions were weak. The circular dichroism of rotational shift around the incident-light axis was observed. Rotational shifts of the FFPs at [1 1 1] and [1 1 1] directions were large, while the FFPs at [1 1 1] and [1 1 1] directions were small. This is because the distance to the scatterer atoms at the former directions are one third of that at the latter directions. These shifts correspond to the parallax in the stereograph of the atomic arrangements of zinc blende structure seen from an In atom. Furthermore, Kikuchi-pattern-like features at the {1 1 1} planes appeared which were absent in the Si 2p PIAD. These features are attributed to the FFPs of atoms within the {1 1 1} and {1 1 1} planes.

3.3 Applications

Stereo atomscope is a direct local atomic structure visualization tool with element selectivity. Like the other photoelectron diffraction based methods, such as energy scan mode EXAFS, photoelectron diffraction [9] and photoelectron holography [41], this method does not require long-range order in the sample. Bi_2Ca_2SrCu_2O_8, a typical high temperature cuprate superconductor, have a 5 times modulated structure along b axis. Sakai et al. have measured Cu 3p PIADs. From the analysis of the elongated FFP along b axis attributed to Bi atom, they have confirmed the modulated structure within BiO layer [51,52]. Another example is the case of bcc Fe deposition on fcc Cu(001) substrate. Face centered tetra-
nal distortion in the Fe epitaxial film had been identified [53]. Such local atomic arrangement distortion can be readily visualized.

Stereo atomscope is also valid for dopant and intercalated guest atom site analyses [19,54]. Recently, it was discovered that a high concentration doping of boron into diamond leads to appearance of superconductivity [55]. One of the central issue was the relation of dopant site and the critical transition temperature. Kato et al. have investigated the dopant site of B-doped diamond (1 1 1) sur-

Fig. 13. (a and b) 2π Steradian In 3d PIADs displayed in stereo projection excited with σ+ and σ− helicity light, respectively. Center and periphery of the pattern corresponds to the polar angle (θout) of 0° and 90° from the surface normal. (c) Circular dichroism pattern. (d) Position of FFPs corresponding to the scatterer atoms within 4 nm distance.

Fig. 14. Azimuthal dependence of In 3d photoelectron intensity at the polar angle of 54.7°.

Fig. 15. In 3d PIADs from a InP(001) surface excited with σ+ and σ− helicity light. Intense peak at the center corresponds to the forward focusing peak at the [1 1 1] and [1 1 1] directions.
Fig. 16. (a) Summed pattern of C 1s photoelectron angular distribution from the diamond (1 1 1) surface excited by cw and ccw helicity light. The kinetic energy was set to 500 eV. (b) Same as (a) but for B 1s.

As described in the earlier section, the FFP intensity in the [1 1 1] and [1 1 1] directions are different if the occupation of emitter atom are different at two sites, $\alpha$ (0 0 0) and $\beta$ (1/41/4 1/4). As shown in Fig. 16, C 1s and B 1s PIADs are similar. They have clarified that the B atoms are substitutionally doped at diamond lattice. Furthermore, they have revealed from the FFP intensity analysis that the occupation ratio of B atoms at two sites, $\alpha$ and $\beta$ are 2:1. This comes from the nonequivalent activation barrier for B atom adsorption during the CVD growth process between $\alpha$ and $\beta$ sites at the (1 1 1) surface.

In the case of d and f core levels, where photoelectron intensity is relatively large, PIAD can be acquired within few second with sufficient signal to noise ratio. Combining with fast helicity switching system, real-time observation of atomic arrangement in order of 1 s or less became possible [20]. Fig. 17 is a series of Cu 3p stereo photograph taken while the sample surface tilt angle was varied. Visualizations of atomic arrangement in time evolutions during phase transitions and surface reactions are the ongoing theme.

Fig. 17. (a and b) Series of Cu 3p PIADs while rotating the tilt angle of Cu(0 0 1) sample excited with $\sigma_+$ and $\sigma_-$ helicity light. (c) Circular dichroism patterns.
4. Valence band photoemission

The electronic and chemical characters of materials are determined mostly by the movement of electrons at Fermi level. Angle-resolved photoelectron spectroscopy in UPS (ultraviolet photoelectron spectroscopy) region is a powerful technique to study such electrons. Using the rule of the energy and momentum conservation in the photoemission process, the valence band structure can be measured directly. The two-dimensional Fermi surface mapping reveals the driving force of the electronic structure phase transition such as charge density wave and superconductivity.

Three-dimensional Fermi surface is visualized by combining two-dimensional photoelectron spectroscopy and energy tunable synchrotron radiation. In principle, we obtain three-dimensional Fermi surface image by stacking a series of PLADs at Fermi level for different $k_z$. Strong modulations in the transition matrix elements affect the photoelectron intensity. By properly evaluating such effects in the Fermi surface mappings and valence band dispersion measurements, atomic orbitals composing valence band can be determined.

The Fermi surface of Cu was studied by this method. It was revealed that the Cu 4p orbitals composing Fermi surface have their axes pointing outward from the $\Gamma$ point [23]. In Fig. 18, the directions of $p_x$, $p_y$, and $p_z$ orbitals are placed in the $[1 0 0]$, $[0 1 0]$ and $[0 0 1]$ directions, respectively. The 4p orbital ratio distribution calculated by using the ab initio code [56] showed good agreement with the present experimental result. Fermi surface is colored according to the 4p orbital ratio distribution. Blue, red and green colors correspond to 4$p_x$, 4$p_y$, and 4$p_z$ orbitals, respectively.

In XPS (X-ray photoelectron spectroscopy) region, Brillouin zone appears within a small solid angle with transition matrix elements roughly constant. By using high angle-resolved electron spectrometer, three-dimensional Fermi surface can be mapped [57]. It is noteworthy that the photoelectron spectroscopy with high photon energy probes intrinsic bulk electronic states [58–60]. On the other hand, we encounter diffraction effects. We discussed in this section that orbital momentum of valence band can be deduced from valence photoelectron angular momentum.

4.1. Transition matrix elements and photoelectron structure factors

Here we start with a transition matrix, $M$, between the initial and the final states under the dipole approximation scheme. The PIAD $I(\theta, \phi)$ is proportional to the square of $M$.

$$I(\theta, \phi) \propto |M|^2 \delta_{E_i} \times \delta_{E_f} \delta_{\mathbf{k}, \mathbf{q}} \cdot \mathbf{G}$$

$$M \equiv \langle f | \mathbf{e} \cdot \mathbf{r} | i \rangle$$

Delta functions ensure the energy and momentum conservation laws. The dipole operator $\mathbf{e} \cdot \mathbf{r}$ can be expressed using spherical harmonics.

$$\mathbf{e} \cdot \mathbf{r} = \sum_{\sigma=\pm 1} \frac{1}{\sqrt{2}} e^{\sigma} \mathbf{Y}_1(\theta, \phi) \cdot \mathbf{r}$$

The initial state $|i\rangle$ having the wave vector $\mathbf{q}$ and energy $E_i$ is written by a Bloch state in tight-binding approximation as

$$|i\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i \mathbf{R} \cdot \mathbf{r}_j} \sum_{\mathbf{q}, \mathbf{E}} \delta_{\mathbf{E}_i} \delta_{\mathbf{E}_f} \delta_{\mathbf{q}, \mathbf{0}} \mathbf{a}_{\mathbf{n}}(\mathbf{q}) \phi_{\mathbf{m}}(\mathbf{r} - \mathbf{R})$$

$$\mathbf{R} \equiv \mathbf{R}_j + \mathbf{q},$$

where $N$ is the total number of atoms, $\tau_n$ is the position vector of the $n$th atom in the $j$th unit cell at $\mathbf{R}_j$. $\phi_{\mathbf{nm}}(\mathbf{r})$ is the $n$th orbital of the $j$th atom, which is the product of a radial function $R_{\mathbf{n}}(\mathbf{r})$ and a spherical harmonics $Y_{\mathbf{m}}(\theta, \phi)$. $\mathbf{a}_{\mathbf{n}}(\mathbf{q})$ is its LCAO coefficient.

The final state $|f\rangle$ with the wave vector $\mathbf{k}$ and energy $E_f$ is also a Bloch state in bulk, and is written as

$$|f\rangle = 4\pi \sum_{\mathbf{q}, \mathbf{E}} \mathbf{f} \cdot \mathbf{r}_j e^{-i \mathbf{F} \cdot \mathbf{r}_j} Y_{\mathbf{m}}^* \phi_{\mathbf{nm}}(\mathbf{q}) \phi_{\mathbf{m}}(\mathbf{r} - \mathbf{R})$$

This Bloch state is seamlessly connected to the plane wave in the vacuum region. In reality, the conduction band structure of solid and surface affects transition probability [61]. Further implementations with aid of theoretical calculations have been reported extensively recently [62–64].

Using above equations for initial and final states, a new formula for matrix elements is derived. $\mathbf{G} = \mathbf{k} - \mathbf{q}$ is a reciprocal vector.

$$M = \frac{1}{\sqrt{N}} \sum_j \sum_{\mathbf{q}, \mathbf{E}} e^{-i \mathbf{G} \cdot \mathbf{q}} \mathbf{a}_{\mathbf{n}}(\mathbf{q}) A_{\mathbf{nm}}(\mathbf{q})$$

$$= \sum_{\mathbf{q}, \mathbf{E}} \exp(-i \mathbf{G} \cdot \mathbf{r}_j) \mathbf{a}_{\mathbf{n}}(\mathbf{q}) A_{\mathbf{nm}}$$

Here, the “angular distribution from atomic orbital ADAO” $A_{\mathbf{nm}}$ is defined as follows [65].

$$A_{\mathbf{nm}} \equiv \langle f(\mathbf{r}) | \mathbf{e} \cdot \mathbf{r} | \phi_{\mathbf{nm}}(\mathbf{r}) \rangle = \sum_{\Gamma = \pm 1} \mathbf{B}_\Gamma \sum_{\mathbf{m'}} m' \sum_{\mathbf{E}} e^{\mathbf{k} \cdot \mathbf{r}} (\phi_{\mathbf{k}}) c^{s}(\Gamma, \mathbf{m'}, \mathbf{m})$$

$$\sigma = m' - m$$

$\mathbf{B}_\Gamma$ is the integral part of transition matrix elements, which is a constant complex number depending on $l$, $\Gamma$ and photon energy. Gaunt coefficient $c^{s}(\Gamma, \mathbf{m'}, \mathbf{m})$ is non zero only when $\sigma = \pm 1$ or $0$.

When the initial state is composed of only one kind of atomic orbital, we can separate ADAO term out of the absolute value as

$$|M|^2 = \sum_n \exp(-i \mathbf{G} \cdot \mathbf{r}_j) \mathbf{a}_{\mathbf{n}}(\mathbf{q}) |A(I, \phi)|^2 = |F(\mathbf{k})|^2 |A(I, \phi)|^2.$$
We introduced here a “photoemission structure factor PSF” $F(k)$ [31] as

$$F(k) = \sum_n \exp(-iG \cdot \mathbf{r}_n) a_n(q).$$

(16)

The term $|F|^2$ is an intensity distribution in a reciprocal $k$ space, which is independent of the kinetic energy of photoelectrons or incident angle of photons. This factor originates from the interference of the photoelectron waves from different groups of atoms in a unit cell and is similar to the structure factors in X-ray or electron diffraction replacing the scattering factors by the coefficients for each atomic orbital in the LCAO wave function [32].

Here, we showed that the PIAD from valence band can be understood in simple cases as a product of band dispersion, PSF, and...
ADAO. In the next section, we will see how these terms act in real systems using the data for single crystal graphite.

4.2. VB photoemission in UPS region

The cross-section of valence band dispersion of graphite along high symmetry plane K Γ M K / H A L H is shown in Fig. 19. Dotted lines are the calculated band dispersion along HALH symmetry directions using a b initio code [56]. The valence band consists of one π band and three σ bands. Energy and the atomic orbital characteristics of these bands obtained from calculation agreed perfectly with the results of experimental investigation discussed below. The π band dispersing from Fermi level down to the binding energy of 8 eV is made of p_y orbitals. Two σ bands from around 5 to 12 eV are made from p_x and p_z orbitals. The σ band from 12 to 20 eV are mainly from s orbitals.

Left and center rows in Fig. 20 are the PIADs of graphite obtained by using He II (40.8 eV) and linearly polarized synchrotron radiation, respectively. Photon energy in the latter case was tuned to 45.2 eV, in order to suppress the effect of Umklapp scattering [66]. The brightness is proportional to the photoelectron intensity. Graphite has honeycomb carbon sheets, and its electronic structure has a six-fold symmetry. Hexagons in Fig. 20 represent the first Brillouin zone of graphite. The center of the hexagon is the Γ′/A point, the apex is the K/H point, and the midpoint of one side is the M/L point as shown in Fig. 20(i).

Photoelectrons at Fermi level shown in Fig. 20(a) and (e) are from vicinity of H points where π bands degenerate. All six points are bright in the case of non-polarized light excitation, but only four of them are observed in the linearly polarized light excitation case. This is due to the characteristics of p_y ADAO shown in Fig. 20(l).

As the binding energy increase to 2.0 eV, π band disperses to M/L points. Six M points appear as bright, however, outside M points in the second Brillouin zones remain dark. This is explained by the PSF of π band shown in Fig. 20(i). Photoelectron intensity along KM/HL lines outside the first Brillouin zone is calculated to be zero, which coincide with the experimental observations. This intensity inequivalency between the first and the second Brillouin zones has a meaning that this π band is a “bonding band”.

From the binding energy of 4.0 eV, σ band appears at Γ′/A point. The π band appearing as a ring-like feature disperses to Γ′/A point, while the σ band disperses toward M/L points. Note that the σ band intensity is observed only at four M/L points in the case of linear polarization as shown in Fig. 20(h). This indicates that the σ band is composed of p_x and p_y atomic orbitals.

The gross feature of the intensity distribution is determined by the ADAO, A_σ, and modified by the PSF. PIAD measurement by the combination of DIANA and a linearly polarized light enables analysis of atomic orbitals and bonding character. From A_σ, atomic orbital consisting band can be determined, while from the PSF, the bonding nature in other word phase relation between atomic orbitals within a unit cell can be deduced [21,31,32].

Even a three-dimensional energy band dispersion structure can be obtained by stacking a series of binding energy scanned PIADs [21]. Based on the three-dimensional energy band data, we can quantitatively analyze the behavior of valence electrons. The group velocity of electron is obtained by differentiating the three-dimensional surface. The electric conductivity or cohesive energy is also obtained by integrating the curved surface. In this way the photoelectron spectroscopy using a DIANA opened new fields of photoelectron spectroscopy.

4.3. VB photoemission in XPS region

Surprisingly, FFPs also appear in the PIAD at high kinetic energy from well delocalized valence band [24–28]. However, the mechanism of FFP formation in the PIAD from valence band has remained unclear. We challenged this issue by measuring the circular dichroism angular distribution (CDAD) of graphite for each band (2p_x, 2p_y, 2s) [29]. As discussed in the previous section a specific pattern in a reciprocal space due to the interference of photoelectron waves excited from several atomic orbitals within a same unit cell, PSF, was observed [31–33,21]. At the same time, we observed significant FFP parallax shifts as in the case of core photoelectrons. Moreover, the parallax shift was found to correlate with the angular momentum quantum number of valence band. Here we discuss the origin of the dual behavior that appeared in the observation of local angular momentum from a delocalized valence band in conjunction with the dispersion and spatial origin of the electron. Fig. 21 depicts the graphite crystal structure. There are two types of atom, namely C_A and C_B. One of the shortest C_A–C_B bond directions is aligned to the x axis. Arrows f_1, f_2 and f_3 indicate the interatomic directions from atom C_A.

The configuration of the Brillouin zones (BZs), the incident light and the screen is shown in Fig. 22. The directions of the k_x, k_y, and k_z axes are along Γ–M, Γ–K, and Γ–A, respectively. Hexagonal tiles in the k_x– k_y plane represent graphite BZs. The hemisphere in Fig. 22 corresponds to the end points of all photoelectron wave vectors with the kinetic energy of 500 eV. The BZ boundary is projected to the hemisphere. Reciprocal unit vectors q_m are defined in Fig. 22. BZ at n q_m _k + n q_m _s is labeled as (mn). Here, we refer to (00), (11), and (22) BZ as ‘odd BZ’ while (10) BZ as ‘even BZ’. Odd BZs are represented with dark colored hexagons while even BZs are represented with light colored hexagons. Odd BZs projected to the screen are rimmed with solid lines.

The PIADs are obtained using σ_+ and σ_− helicity light. In Fig. 23(a)–(c), the PIADs of the graphite valence band excited with both σ_+ and σ_− helicity light are summed, while those of (d)–(f) are the difference of them. The midpoint of the top side is the Γ point of (00) at the surface normal direction. The photoelectron kinetic energies were 484.5 eV in (a) and (d), 476.4 eV in (b) and (e), and 468.5 eV in (c) and (f). Hexagons superimposed represent the boundaries of odd BZs. The PIAD in Fig. 23(a) has a slight modulation. As the kinetic energy decreases and the larger binding energy level is probed, the intensity at the boundary of BZ markedly increases [Fig. 23(b)]. Furthermore, at the kinetic energy of 468.5 eV, photoelectron intensity maxima appear at the center of odd BZ [Fig. 23(c)].
Fig. 22. Orientation of Brillouin zone (BZ) and the screen. Axes $k_x$ and $k_y$ are along $\Gamma$–M and $\Gamma$–K directions, respectively. Circularly polarized light ($h/\mathbf{ETB}$) is incident along the $z/k_z$ axis. The radius of this hemisphere represents the absolute value of the photoelectron wave vector at a kinetic energy (KE) of 500 eV. Graphite BZs indicated by hexagonal tiles in the $k_x$–$k_y$ plane are projected to the hemisphere and the screen.

Fig. 23. Summed (a)–(c) and differential (d)–(f) PIADs of graphite valence band excited with $\sigma_+$ and $\sigma_-$ helicity light at various kinetic energies (KEs) and binding energies (BEs). Hexagons superimposed represent the boundaries of odd BZs. Prominent circular dichroism features labeled A–D are circled with broken lines.

Fig. 24. Graphite valence band energy distribution curve at the high symmetric points in BZ (marks) and the total intensity of all PIADs (solid line).

4.3.1. Photoelectron structure factor

This phenomenon is more clearly seen by comparing the energy distribution curve at each $k$ point. The solid line in Fig. 24 is the energy distribution curve of the graphite valence band obtained by summing all PIAD intensities. Assuming a work function of $\sim$0.5 eV, the Fermi level is estimated to be at $\sim$495.5 eV. The 2p$_z$ band disperses from the Fermi level to a binding energy of 10 eV, while the 2p$_{xy}$ band disperses from 5 to 15 eV. The 2s band extends from 15 to 25 eV. The observed band width is broadened due to the low energy resolution in this experiment.

Open and solid circles in Fig. 24 are the averaged $\Gamma$/$\Lambda$ point intensities of odd ((1 1), (2 2), (3 1), and (1 3)) and even ((0 2), (2 0), (1 2), and (2 1)) BZs, respectively. Note that the former is much larger than the latter at a binding energy of 25 eV where 2s band dispersion has its bottom at $\Gamma$/$\Lambda$ (Fig. 23(c)). At 18 eV, where 2s and 2p$_{xy}$ bands disperse to K/H and M/L points, the intensity at the $\Gamma$/$\Lambda$ point is the lowest and the intensities from K/H (indicated by $\Delta$) and M/L (+) points are large (Fig. 23(b)).

Intensity inequality observed at $\Gamma$/$\Lambda$ points of odd and even BZs in Fig. 23(c) can be explained by PSF [31–33]. PSF represents the interference of photoelectron waves from different atomic orbitals of the valence band within a unit cell. A graphite unit cell includes two kinds of carbon atoms labeled $C_A$ and $C_B$ in Fig. 21. For example, two kinds of the 2s atomic orbital in a bonding configuration form 2s band. The photoelectron waves propagating from both orbitals undergo constructive and destructive interference in even and odd BZs, respectively. Fig. 23(c) corresponds to such an interference pattern. It is the same for the 2p$_z$ band. The photoelectron waves of the 2p$_{xy}$ band undergo constructive and destructive interference in odd and even BZs. At the binding energy of 10 eV, the 2p$_{xy}$ band disperses toward $\Gamma$/$\Lambda$ point. Here, the bottom of the 2p$_z$ band at the $\Gamma$/$\Lambda$ point is not so different.

4.3.2. Parallax circular dichroism

In each CDAD pattern ($I(\sigma_+) - I(\sigma_-)$) shown in Figs. 23(d)–(f), pairs of maxima and minima are observed. These prominent CDADs are circled with broken lines and labeled $\Lambda$–$\Delta$. CDAD $\Lambda$ appeared at the polar emission angle $\theta$ of 54° while $\Sigma$ and $\Delta$ appeared at 45° and 23°. Note that CDADs $\Lambda$, $\Sigma$, and $\Delta$ correspond to the interatomic direction of two $C_A$ atoms belonging to the different layers, that are indicated in Fig. 21 by arrows $f_1$ and $f_2$, respectively. In the directions of $f_1$ and $f_2$ seen from $C_B$ atom, there are no corresponding atoms. CDADs $\Lambda$ and $\Sigma$ originate from the rotation of FFPs produced by the interatomic relationship between two $C_A$ atoms, but not $C_B$ atom. In the directions of $\Sigma$ and $\Delta$, FFPs from $C_B$ atoms overlap in
addition. The FFP shift can be used as a probe for the orbital angular momentum quantum number of different bands at a specific atom in principle.

The FFP rotation showed a strong correlation with the orbital angular momentum of the valence band at each binding energy. The PIAD measured at the binding energy of 9 eV corresponds to the cross-section of the 2p band. The angular interval of maximum and minimum positions was $8^\circ$. At a binding energy of 15 eV, where the 2p$_{xy}$ band is dominant, CDAD intensity becomes significant with an angular interval of $16^\circ$. The PIAD measured at a binding energy of 25 eV corresponds to the cross-section of the 2s band. Again, maximum and minimum come close together ($10^\circ$ apart) and CDAD intensity decreases. From the quantitative analysis [29], $m$ determined from FFP rotational shift $\Delta \phi$ for the 2s and 2p$_x$ bands was $\pm 1.0$ while it was $\pm 2.0$ for the 2p$_{xy}$ band. Hence, this observation of the CDADs of FFP indicate that the 2p$_x$ and 2s bands have orbital angular momentum of 0 and that 2p$_{xy}$ has that of 1, which correspond to our knowledge.

In addition, diffraction effects in FFP can be removed by normalizing rotational angle by that of the core-FFP measured at same kinetic energy [30]. The effective angular momentum for core-level photoelectron is determined explicitly, since core-level is fully occupied. By the normalization, diffraction effect has been cancelled out, and reasonable angular momentum of Fe valence band has been obtained [30].

Now, we discuss about the origin of the dual behavior of FFPs in valence-band PIAD, which has been under long debate. Osterwalder et al. reported that the maxima observed in the Al(001) valence-band PIAD excited by Mg K $\alpha$ (1254 eV) very closely resemble FFPs in the 2s PIAD [24]. However, the mechanism of FFP formation in the valence-band PIAD has remained unclear. Osterwalder et al. postulated a localization of the hole left behind by the photoelectron at a single atomic core site [24,67]. Subsequently, Sarma et al. argued that the reason was the complete zone averaging caused by the limited angular resolution and the energy integration [68]. The zone averaging induced by the phonon excitations during the photoemission was proposed as an alternative explanation [25,69]. On the other hand, Solterbeck demonstrated with one-step-model calculations that the spatial origin of the photoelectron is localized at the core in the high-kineic-energy region [70].

The observation of the dual behavior of FFP (which originates from a local effect) and PSF [31–33] (which is a result of delocalization) in valence-band PIAD is the important clue. Here, we propose an explanation. The initial state is given by a Bloch function, which is a coherent sum of atomic orbitals over every lattice site $R$. The outgoing-photoelectron wavefunctions from each site scattered by neighboring atoms $\tau_n$ are coherently summed resulting PIAD.

$$I(\theta, \phi) = \left| \sum_j \psi_{R_j} \right|^2 = \left| \sum_j (\psi_{R_j}^0 + \sum_n \psi_{\text{scat}}^{\tau_n-R_j}) \right|^2$$

The outgoing-photoelectron wavefunctions from single atomic orbital $\psi_{R_j}^0$ is equivalent to ADAO, $A_{R_j}$. In the present case, PSF appears in addition after the summation of $\psi_{R_j}^0$ from every lattice site. On the other hand, observed FFP, is the summation of local scatterings $\psi_{\text{scat}}^{\tau_n-R_j}$ at every lattice site.

A clear FFP can only be created by spatially localized initial state around an emitter atom, which has been discussed by Solterbeck et al. [70]. This localization can easily be understood by considering the spherical Hankel function of the first kind $h_0^{(1)}(kr)$ representing the outgoing wave $\psi_0$ from the emitter atom in the final state. The maximum transition probability is located at approximately $m/k$ away from the emitter atom, which corresponds to the impact parameter $b [14,4]$. In the present case, $b = m^2/k \sin \theta$ is about 0.2 Å for $\theta = 54^\circ$.

Very recently, the indication of recoiled atom motion in hard X-ray photoemission process is reported for C 1s core-state excitation in graphite [71,72]. This phenomena is even observed in the case of valence excitation at Fermi level of simple metals [73]. The local excitations of delocalized states can be understood by above explanation.

In conclusion of this section, the information contained in PIAD measured in UPS region has been described. The symmetry relation in the photoelectron excitation process is observed as "angular distribution from atomic orbital ADAO". By using a linearly polarized light, the atomic orbital constituting the energy band can be deduced. Another important angular distribution is the "photoemission structure factor PSF", which originates from the interference among photoelectron waves from individual atoms. PSF determines the intensity inequivalency between Brillouin zones and reveals the bonding character of the energy band or the phase relation between atomic orbitals. Energy band dispersion and atomic orbital information can be mapped in a three-dimensional $k$ space by scanning the photon and binding energy. The complementary method of the atomic orbital analysis using linearly polarized light [21,23,74] was proposed. The FFP parallax shift in the valence PIADs appeared in XPS region. Since FFP is a site-specific probe, the orbital angular momentum of valence electron at a local site can be deduced in principle.

5. Diffraction spectroscopy

As the last topic, we introduce a new method of disentangling spectra from different atomic layers by use of Auger electron diffraction. Taking advantage of the FFP as an excellent element- and site-selective probe, diffraction spectroscopy enables direct access to the electronic and magnetic structures at subsurface region. This new concept is compared with a conventional spectro-diffraction method. Application of this method for studying the electronic and magnetic structures of Ni thin film at atomic level is presented [34]. Lastly, we conclude with a discussion on the perspective of this method.

5.1. Spectro-diffraction

ESCA, electron spectroscopy for chemical analysis, is a name given for core-level photoelectron spectroscopy [75]. Combined technique, ‘spectro-diffraction’ is used for a chemical state selective structure analysis [76–78]. Here, one example of surface structure investigation using conventional energy dispersive electron analyzer is shown. The atomic structure of the Nb(1 1 0) surface with oxygen segregated from bulk by annealing at 1500 K in UHV has been studied by $2\pi$ steradian X-ray photoelectron spectro-diffraction [79].

Fig. 25 shows Nb 3d core level photoelectron spectra from the Nb(1 1 0) surface after annealing. Peaks at 197.2 and 199.9 eV corresponding to 3d$^5/2$ and 3d$^3/2$ levels of Nb atoms in bulk is fitted with Gaussians having width of 1.65 eV. Branching ratio between observed 3d$^5/2$ and 3d$^3/2$ peaks was 0.63 which is close to 2/3 expected from spin–orbit occupation numbers. Another set of Gaussians shifted 1.6 eV to higher binding energy was needed for the fitting. Chemical shift of 1.6 eV corresponds to the oxidation number of Nb in NbO [80]. Lower panel shows a surface-sensitive Nb 3d spectra taken at the emission angle of $60^\circ$ off from surface normal. Since peaks at 198.8 and 201.5 eV appear larger in the lower panel, they are attributed to Nb atoms in surface overlayer. The Nb surface overlayer is estimated to be 4.5 Å thick, that is roughly equal to one or two atomic layers.

Fig. 25 shows Nb 3d core level photoelectron spectra from the Nb(1 1 0) surface after annealing. Peaks at 197.2 and 199.9 eV corresponding to 3d$^5/2$ and 3d$^3/2$ levels of Nb atoms in bulk is fitted with Gaussians having width of 1.65 eV. Branching ratio between observed 3d$^5/2$ and 3d$^3/2$ peaks was 0.63 which is close to 2/3 expected from spin–orbit occupation numbers. Another set of Gaussians shifted 1.6 eV to higher binding energy was needed for the fitting. Chemical shift of 1.6 eV corresponds to the oxidation number of Nb in NbO [80]. Lower panel shows a surface-sensitive Nb 3d spectra taken at the emission angle of $60^\circ$ off from surface normal. Since peaks at 198.8 and 201.5 eV appear larger in the lower panel, they are attributed to Nb atoms in surface overlayer. The Nb surface overlayer is estimated to be 4.5 Å thick, that is roughly equal to one or two atomic layers.
Fig. 25. Nb 3d core-level photoelectron spectra from the Nb(1 1 0) surface after annealing up to 1500 K. Al Kα radiation was used for the excitation. Light and dark hatched peaks correspond to bulk and surface components, respectively.

Fig. 26. Nb 3d PIADs. 4945 Different spectra were fitted by bulk and surface components. Their intensity angular distributions are plotted as (a) and (b), respectively. Coordinates are depicted in (c). The structure models of (d) the Nb(1 1 0) surface and (e) the NbO overlayer. Dimensions indicated are those from bulk Nb and NbO crystals. The arrows indicate the typical directions of FPP observed in PIADs.

Nb 3d spectra were measured for the polar emission angle range from \( \theta = 0^\circ \) to \( 78^\circ \) with a step of \( \Delta \theta = 3^\circ \) and over the 360º azimuthal angle range with a step of \( \Delta \phi \cdot \cos \theta \approx 1^\circ \). Monochromatized Al Kα (1486.7 eV) source and spectrometer (VG ESCALAB5) were fixed while the orientation of sample mounted on 5-axis manipulator were varied. Intensities of the Nb 3d peak were collected at 4945 different directions. The intensity was normalized by a detection geometry factor of \( \cos \theta \).

Each spectrum was fitted with a combination of Gaussians and an integral background of the Shirley type using above mentioned parameters in Fig. 25. Full solid-angle PIADs for each Nb 3d component by separating the observed 3d spectra into bulk and oxide components by curve fitting are obtained as shown in Fig. 26(a) and (b), respectively. The orthographic projection method was used to plot these data. The direction of the high-symmetric axes are indicated in Fig. 26(c). The horizontal direction is [0 0 1] and the vertical direction is [1 1 0]. High and low photoelectron intensities are expressed as white and black, respectively. No symmeterization process was applied.

Fig. 26(a) is a typical bulk single-crystal PIAD, showing strong FPPs along low-index directions, as well as Kikuchi bands connecting these directions. Center spot corresponds to a FFP at [1 1 0]. The directions of the strongest peaks defining the parallelogram near the center of the PIAD are [1 0 0], [0 1 0], [1 1 1] and [1 1 0]. Fig. 26(b), for emission from Nb atoms bonded directly to oxygen atoms, shows six peaks at azimuths at \( \phi = \pm 31.1^\circ \) and \( \phi = 90^\circ \) off from [0 0 1] direction. Polar angle was about 60º off from surface normal direction.

Arfaoui et al. have reported the observation of a quasiperiodic arrangement formation of nanosize NbO crystal on the Nb(1 1 0) surface [80]. They attributed the origin of its mechanism to a mismatch at the interface between the fcc NbO thin film and the bcc Nb substrate. However the local atomic structure was unclear. Chemical environment selective PIAD permits a determination of the adsorbate position directly. The PIAD from the surface core-level shifted Nb 3d peak associated with Nb atoms directly bound to O showed six FPPs. From this data the position of oxygen has been estimated to be 1.2 Å above the first-layer Nb atoms and bound triply to Nb atoms in a hollow site.

By using a spectrometer of state-of-art, spectro-diffraction enables a detailed structure analysis of well defined surfaces. However, the drawback due to the sample-rotation procedure is the tremendously long data acquisition time (it took 500 h for the above case). It is not preferable for the measurement of inhomogeneous structured and/or unstable samples.

5.2. Resolving subsurface magnetism

Future data storage densities will soon need to exceed one terabyte (10¹² bytes) per square inch, requiring bits just 10 nm or less across. But this is the scale at which surface magnetism becomes dominant. So it is critical to understand unusual magnetic effects from a nanoscopic point of view. The magnetism of the outermost atoms can be detected individually by means of magnetic STM [81], whereas much difficulty lies in the case of subsurface atoms. So far, several methods have been developed for probing the magnetic structure of the buried interface and multilayers [82,83]. But the atomic level characterization technique for subsurface magnetic structure did not exist up to now. Recently, Amemiya et al. have succeeded in evaluating magnetic moments of surface and subsur-
face by using emission angle dependence of Auger electron probing depth [84,85]. However, atomic layer resolution which is essential for the understanding of SRT and the quantitative comparison with the theoretical studies [86] was not realized in their work. Here we report a direct method for such purpose.

We combined two existing techniques: X-ray absorption spectroscopy and Auger electron diffraction (AED). X-ray absorption near edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) measurements by Auger electron yield detection are powerful analysis tools for the electronic and magnetic structures of surfaces. However, all the information from atoms within the electron mean-free-path range is included in the obtained spectra. FFPs in AED patterns indicate the directions of atoms surrounding the excited atom. Taking advantage of the FFP as an excellent element- and site-selective probe [29,97], we disentangled spectra from different atomic layers.

The details of Ni film atomic structure are still unclear. The layer-by-layer growth mode of Ni film was confirmed by STM [87], but due to the lack of element specificity and atomic resolution in depth direction, it has been a long-debated issue whether Ni interlayer mixing occurs or not at the initial growth stage [88–90]. New interlayer mixing model at the interface was recently proposed by means of X-ray diffraction [91]. The easy magnetization axis turns from in-plane to perpendicular direction at 10 monolayers (ML). Perpendicular magnetization appears in a wide thickness range, up to 40 ML, then again turns back to in-plane magnetization [92–94]. Surface magnetism manipulation at the vicinity of SRT through chemical modification [95] precluded the existence of a spin dead layer [96], though it is still an open question at the low thickness regime.

5.2.1. Atomic and electronic structure

For the thickness dependence measurements, Ni wedged films with the maximum thickness of 5–20 ML on a clean Cu(001) surface were prepared. The Ni LMM AED pattern in Fig. 27(a) was excited with normal incident soft X-ray (852.8 eV). Typical acquisition time for an AED pattern was 1 s. Fcc cluster shows the relation of crystal orientation and FFPs. Pronounced FFPs appear along the directions of atoms surrounding excited atom in the AED pattern [41]. The FFPs at [10 1] and [00 1] directions indicate the existence of Ni atoms at the second and third layers, respectively. The intensity at an extremely low emission angle especially at [1 0 0] direction is mainly due to the emission from the outermost surface atoms [98,99].

By scanning the position of wedged Ni film, the Ni LMM AED snapshots (kinetic energy of 841.0 eV) from various film thick-
nesses were measured in a short time. This can not be done by conventional apparatus which detects emitted electrons only in one direction at a time and requires sample rotation.

The four-fold symmetry operation is applied to each pattern to obtain 2$\pi$ steradian angular distribution as shown in Fig. 28. Note that the [1 0 1] FFPs from the second-layer atoms and the [0 0 1] FFP from the third-layer atoms are weak but already present in the 1 ML and 2 ML AED patterns, respectively. This is a direct evidence of an interlayer mixing of Ni atoms and Cu topmost surface atoms. On the other hand, Kikuchi bands become apparent from 4 ML AED pattern indicating fcc-like epitaxial growth in spite of a 2.5% misfit between the Ni and Cu lattice constants. Cu atoms segregated to the top layer at the initial stage probably act as a surfactant to relax the film stress in the subsequent epitaxial growth process [94,100].

Auger electron yield is proportional to the number of core-holes created by photon absorption. XANES spectrum is obtained by monitoring Auger electron intensity while scanning the excitation photon energy. Since a core-state electron is excited to the conduction band with photon energy beyond the absorption threshold, XANES represents the partial density of the unoccupied state. The combination of the AED method and the XANES measurement opens a new way to investigate the layer-selective electronic structure at surfaces [52]. We measured thickness dependence of XANES by taking a series of Ni LMM AED patterns at various sample positions as shown in Fig. 29.

The intensity of different FFP corresponds to the signal from different atomic layers. Fig. 30(a) shows the atomic-layer resolved Ni L$_3$-XANES spectra from the various thickness of the Ni wedged thin film. The first, second, and third layer spectra were extracted from [1 0 0], [1 0 1], and [0 0 1] FFP intensity, respectively. Uniform elastic scattered background signal was eliminated by subtracting intensity of the surrounding region shaded by light blue in the AED patterns indicated in Fig. 27(b). The L$_3$ peaks in the spectra from the surface layer shift to higher photon energy compared to that of interior layers.

L$_3$-XANES spectra were fitted with Gaussian peaks and step functions. Intensity around [1 0 3] direction in the thick film AEDs was referred as a bulk signal. Fig. 30(b) summarizes peak shifts for each component from various film thicknesses. The surface layer Ni L$_3$ absorption peak from 3 ML Ni film shifts to higher energy by about 100 meV compared to those of the third layer. L$_3$ shifts correspond to the surface core-level shifts. The large shift of 360 meV observed for the 1 ML spectrum can be explained by the charge transfer to the substrate and segregated Cu atoms [100]. The layer specific core-level shift depicted in Fig. 30(b) reveals that surface from the electronic structure point of view is just 3 ML thick in the metal case owing to the screening by valence electrons.

5.2.2 Magnetic structure

Then, we magnetized the Ni wedged film along surface normal direction and measured XANES and XMCD spectra for various film thicknesses with remanent magnetization. The AED patterns in Fig. 27(b) indicate the FFP regions corresponding to the signal from each layer. Ni L$_3$-XANES from the 8 and 15 ML films are shown in Fig. 31(a). The second, third and fourth layer spectra were extracted from [1 0 1], [0 0 1], and [1 0 3] FFP intensity, respectively. In the case of 15 ML, the spectrum of the surface layer was extracted from [1 0 0] FFP intensity. Note that so-called 6-eV satellite is diminished in the surface layer spectrum [85,101]. Vanishing of the 6-eV satellite is due to the atomic and electronic structures peculiar to the outermost surface layer where atoms bond to the relatively few neighboring atoms [85].

XMCD spectrum is the difference of the Ni L$_3$-XANES spectra excited with $\sigma_+$ and $\sigma_-$ helicity light. Fig. 31(b) shows the atomic-layer-resolved XMCD spectra for the 8 ML and 15 ML films. In the case of 8 ML, large XMCD appeared in the 45$^\circ$ incidence geometry but did not appear in the normal (0$^\circ$) incidence geometry. This polarization dependence indicates that the Ni thin film is magnetized in plane. In the case of 15 ML, polarization dependence that indicates perpendicular magnetization was observed. Here, normal incident spectra are shown. Surface layer XMCD from the 15 ML had similar intensity as that of the 8 ML, while the XMCD from the subsurface layers drastically increased.

Here we analyzed the magnetic structures of the in-plane and perpendicularly magnetized Ni thin films in atomic scale. Fig. 32
summarizes the spin ($\mu_{\text{spin}}^{\text{eff}}$) and orbital ($\mu_{\text{orb}}$) magnetic moments for each atomic layer deduced from standard sum rule analysis [102–104]. Values of magnetic moments for the in-plane magnetization were multiplied by a factor of $\sqrt{2}$ in order to take the 45° incidence measurement into account.

Spin magnetic moments deduced here are small compared to the bulk value of 0.5 $\mu_B$ [101]. This estimation is consistent with the reported values for the outermost layer by experiments [84] and the overlayer by theoretical calculations [86]. Note that the orbital magnetic moments are more enhanced at the surface layers compared to the spin magnetic moments in the case of 8 ML (in-plane), while variations of the moments are rather small in the case of 15 ML (perpendicular). The orbital is sensitive to the local bonding configuration, while the spin reflects the long range magnetic ordering. The present data suggest that at a thickness beyond SRT, the magnetic moment orientation in a perpendicular direction is caused by the spin magnetic moment in the interior layers, whereas at the region below SRT, where the spin magnetic moment is small, the orbital magnetic moment at the surface layers determines the orientation to be in-plane. SRT at 10 ML is based on such a subtle balance of magnetic moments.

5.3. Perspectives

A newly developed technique, diffraction spectroscopy enables direct access to the subsurface atoms, which connects surface and bulk worlds [34]. Now surface and interior core-level shifts and magnetic moments can be determined for each atomic layer individually. This method can also be applied to layer-specific analysis for anti-ferromagnetism and spin density wave. By means of conventional spectroscopic methods, all the information from atoms within the electron mean-free-path range is averaged into the obtained spectra and the signal having such oscillatory behavior is vanished.

XANES measurement combined with AED has been utilized to examine depth profile of the carrier density in conduction state for copperate superconductor [52]. Application to the study of surface reaction is underway. The electronic state of molecular adsorbate and dissociated species are investigated separately. Furthermore, by extending the range of photon energy scan, combined method of EXAFS and AED is achieved, which is expected to be a bond-selective structure determination method. The concept of diffraction spectroscopy is not restricted to Auger electron yield measurements. Combination with a photoelectron spectroscopy of constant final state mode with PIAD is effective for the layer dependent atomic composition analysis.

6. Summary

Photoemitted electrons from solids carry lots of the information with them. For the interpretation of photoelectron intensity, it is
essential to understand the effect of complicated interplay between photons, electrons and atoms. Often we can not see the forest for the tree. By analyzing entire PIADs, these effects are well separated and useful information can be obtained. A new methodology is developed by adding one more dimension. We have shown that the electronic and magnetic properties can be investigated in atomic scale. Principles and applications of direct atomic structure analysis by stereo atomoscope have been shown. Valence-band angular momentum analysis by circularly polarized light photoelectron diffraction was reviewed in comparison with atomic orbital analysis by linearly polarized light two-dimensional photoelectron spectroscopy. Finally, perspectives of atomic-layer-resolved magnetic structure analysis by diffraction spectroscopy have been discussed.

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