Stereo-microscopy of atomic arrangements on thin films using circular dichroism in x-ray photoelectron angular distribution

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We present a new direct method of “stereo-microscope” for three dimensional structure analysis of thin films, with which one can realize three-dimensional atomic arrangement directly by eyes. The azimuthal shifts of forward focusing peaks in photoelectron angular distribution pattern obtained with left and right helicity light are the same as the parallax in stereo-view. Taking advantage of this phenomenon of circular dichroism in photoelectron angular distribution, one can realize a stereoscope of atomic arrangement. A display-type spherical-mirror analyzer can obtain stereoscopic photographs directly on the screen without any computer-aided conversion process. Some recent results are described.

Key words: structure analysis, photoelectron angular distribution, circular dichroism, stereo microscope, display-type spherical-mirror analyzer

1. Introduction

Nano-thickness of thin ferromagnetic layer on different material surface shows different magnetic behavior than its bulk. For example the Ni film on Cu(001) surface shows non-magnetization below few monolayers (ML), magnetization parallel to the surface between 4 to 7 ML, perpendicular to the surface between 7 to about 37ML, and then again change to parallel to the surface3). In the case of Fe on Cu(001), the first magnetization is strong perpendicular one until 4 ML, then weak perpendicular until 10 ML, and parallel after 10 ML2). The mechanism of these spin-reorientation transitions (SRT) has been discussed by considering the competition among a magnetoelastic volume anisotropy due to pseudomorphic growth, the shape anisotropy and the sum of the surface plus interface anisotropies which favor in-plane magnetization1). The Fe film on Cu(001) is thought to change from fct structure, to fcc structure, and finally to bcc structure3). These structure changes may explain the SRT. The structure analysis of these films has been made using LEED, RHEED, STM, and so on. However, these methods are not direct method to reveal the three-dimensional atomic arrangement, and some ambiguity remains. Here we describe a new direct method of three dimensional structure analysis of thin films, with which one can realize three-dimensional atomic arrangement directly by eyes.

The azimuthal shifts of forward focusing peaks in photoelectron angular distribution pattern obtained by left and right helicity light are found to be the same as the parallax in stereo-view. Taking advantage of this phenomenon of circularly-polarized-light photoelectron angular distribution, one can realize a stereoscope. A display-type spherical-mirror analyzer2,3) can obtain stereoscopic photographs directly on the screen without any computer-aided conversion process. Because the stereo photographs are presented directly on the screen, real time observation is possible when the switching rate of the helicity is fast. By selecting the kinetic energy of photoelectrons, the photographs become element- and chemical-state- selective. Because this method is a microscope, even single molecule could be viewed in principle.

2. Display-type Spherical Mirror Analyzer

The measurement was made using a display-type spherical mirror analyzer (DIANA). G: hemispherical grid, Ob: obstacle rings, Os: outer sphere, Gd: guard rings, O: the center of the hemisphere, S: sample, A: exit aperture, R: retarding grid, M: pair of microchannel plates (MCP), P: phosphor screen, SR: synchrotron radiation, L: lens, E: electron gun, D: deflector, PG: pre-acceleration or retardation grids. The angular distribution of photoelectrons of one particular kinetic energy from S is displayed on P without distortion.

Fig.1 Display-type spherical mirror analyzer (DIANA). G: hemispherical grid, Ob: obstacle rings, Os: outer sphere, Gd: guard rings, O: the center of the hemisphere, S: sample, A: exit aperture, R: retarding grid, M: pair of microchannel plates (MCP), P: phosphor screen, SR: synchrotron radiation, L: lens, E: electron gun, D: deflector, PG: pre-acceleration or retardation grids. The angular distribution of photoelectrons of one particular kinetic energy from S is displayed on P without distortion.
spherical mirror analyzer (DIANA) (Fig.1), which was invented in 1988\(^3\) and gradually improved\(^4\)-\(^6\). Comparing with Eastman-type display analyzer\(^7\),\(^8\), this analyzer has two advantages. One is that the angles of emission and detection of photoelectrons are exactly parallel; hence the pattern displayed on its screen is not distorted. The other is that the acceptance angle can be made infinitely wide, because the convergence to the exit aperture is exact irrespective of the angle and has no higher order terms. Hence one can measure the angular distribution of particles of one particular kinetic energy up to about 2\(\pi\) steradian at a time. In the development of the analyzer, the energy analysis method has been changed from “focus-defocus”\(^3\) to “high-pass and low-pass filter”\(^4\),\(^5\). The energy resolution of the conventional DIANA has been about 1\% of the pass energy.

Fig.1 shows a schematic view of the new display-type spherical mirror analyzer\(^9\),\(^10\). The number of obstacle rings Ob and guard rings Gd are 260 and 20, respectively. The Ob’s are axially symmetric with respect to the axis connecting the sample and the center O of the hemisphere, and their inner surfaces are a part of concentric spheres. G is usually grounded. The potential \(V(r)\) of Ob’s and guard rings are biased according to their radii \(r\) from O by a formula \(V(r) = 2E_0(1 - a/r)\), where \(E_0\) is the pass energy and \(a\) is the radius of the main grid G. The electrostatic field in the space surrounded by the electrodes G, Ob and Gd is thus made spherically symmetric with respect to the center O. The orbits of the emitted electrons from the sample S are subjected to this field after passing through G, and their loci are ellipsoids obeying the Kepler’s law. Their trajectories inside G are straight lines.

The electrons converge exactly to the exit aperture A, which is located at the symmetric position of S with respect to O. Their incident angles are exactly parallel to their emission angles. Ob’s play essential roles in energy analysis by cutting unnecessary electrons that have higher kinetic energies than the pass energy \(E_0\). An electron having a little higher energy flies along a little outside locus and hit into the electrodes and absorbed or scattered, and hardly passes through the small aperture A. Thus the Ob’s work as a “low-pass filter”. On the other hand, the retarding grid R works as a “high-pass filter” which retards the electrons having lower kinetic energies than the applied potential.

The electrons having passed through the retarding grid are amplified by a pair of microchannel plates (MCP) M and converted by a phosphor screen P to light pulses, which are detected from outside the vacuum chamber by a cooled CCD camera. The two-dimensional angular distribution (2DAD) on the screen is the same as the original 2DAD in front of the sample. An electron gun E is mounted for the purpose of LEED measurement. Synchrotron radiation SR is introduced through a hole. The acceptance cone covered by the MCP is \(\pm 60\) deg. This acceptance angle can be increased up to \(\pm 80\) deg by using the lens L. The diameter of the main grid was two-times enlarged from 150 mm of the old analyzer to 300 mm. The shaping accuracy of Ob was intended to be within 50 \(\mu\)m. The energy resolution \((\pm E/E_{\text{pass}})\) and angular resolution of the present analyzer has been estimated to be 0.25\% of the pass energy and 0.6 deg, respectively.

![Fig. 2 Schematic diagram of photoelectron angular distribution](image)

![Fig. 3 Rotation of forward focusing peaks excited by (a) linearly polarized (LP), (b) left circularly polarized (LCP) light. The six forward focusing peaks in (a) rotate to ccw direction in (b).](image)

When the kinetic energy of a photoelectron is higher than several hundred eV, a strong forward focusing peak appears along the direction connecting the emitter and the scatterer.

3. Peak Rotation in Circularly Polarized-Light Photoelectron Angular Distribution

In general, a forward focusing peak has information about the direction from the emitter to the scatterer but does not have the information about the distance between them. Recently, it was found that the forward-focusing peak-positions in a 2DAD pattern excited by a circularly polarized light rotate in the same direction as the rotation of the electric vector of the light\(^9\),\(^10\). This is a strong circular dichroism in 2DAD for non-chiral and non-magnetic materials.

Figs. 3(a), and (b) are examples of this circular dichroism\(^10\). The six peaks are the forward focusing peaks of the W 4f photoelectrons, from only the first layer W atoms on W(110)\(_{1\times 12}\)-O surface\(^10\). The photoelectrons from the first layer W atoms are easily distinguished from those of bulk W atoms utilizing a large chemical shift (0.73...
eV). Here the photoelectron kinetic energy is 317 eV. The photon was incident normal to the surface. Fig. 3 is plotted by stereo-projection method. The center of the pattern corresponds to the surface normal direction and the edge corresponds to the polar angle of 90°. The polar take-off angle range observed is from 61.0° to 73.5°. We can see six strong forward focusing peaks. The directions of these peaks correspond to the directions of oxygen atoms seen from the first-layer W atoms in two domains[15].

Figs. 3(a) is the result of linearly polarized (LP) and (b) is of left circularly polarized (LCP) light. Here the definition of LCP is that the rotation direction of the electric vector of the photon in the plane of Fig. 3(b) is counter-clockwise (ccw). Because the emitter atom is the top layer W atom and there are only O atoms above it, these forward peaks are considered to be dominated by single scattering. It is clear that there is a tendency for the pattern to shift counterclockwise with LCP excitation in Fig. 3(b).

All these shifts are considered to be a rotation of the forward focusing peaks with respect to the photon incident direction ([110] axis). Such peak "rotations" are of the same qualitative type as seen for Si(001)[9], which was found recently in the photoelectron diffraction patterns from non-chiral and non-magnetic systems. This rotation has been explained as being due to the transfer of the angular momentum of photons to the photoelectrons, whose z component ratio has been biased while being excited by the circularly polarized light.

4. Orbital Angular Momentum of Photoelectron

The characteristic feature of the photoelectrons excited by a circularly-polarized light is that it has an orbital angular momentum around the incident light. A circularly polarized light with the angular momentum of photon $\sigma_{h\nu}$ of ±1 excites the ground state with the magnetic quantum number $m'$ to the final state with $m = m' ± 1$. In other words, the angular momentum that the electron gains in photoexcitation is ±1.

We consider the photoelectrons $\Psi_f$ with the quantum number of the angular momentum $l$ and its z-component $m$. Its angular part can be described by a spherical harmonic $Y_{lm}(\theta, \phi)$. The quantum axis (z-axis) is the traveling direction of the incident circularly polarized light. The final state wavefunction outside the emitting atom is expressed as

$$ \Psi_f \propto e^{ikr} Y_{lm}(\theta, \phi) $$

where $\Theta_{lm}(\theta)$ is the $\theta$ -function in the spherical harmonic.

The propagation direction of this final state wavefunction is intuitively calculated considering the wave front of eq.(2). The phase of the wave is expressed as
The equation of constant phase surface is expressed as
\[ r = -\frac{m\phi}{k} + C \]  
where \( C \) is a constant. This curve is a spiral, and shown in Fig. 5 by solid and broken lines. The wave propagates perpendicular to these lines, which is the wave front, as shown by thick arrow in Fig. 5. The shift of the forward direction \( \Delta \) from OA direction is expressed by eq. (1).

The physical base of the azimuthal shift is summarized as follows. The forward focusing peak appears because the phases of all wavelets on the wave front being scattered by each infinitesimal atomic potential coincide in the forward direction. This "forward direction" is perpendicular to the wave front of the wave. When the wave has as angular momentum, the wave front hit the scatterer at an angle. Hence the forward direction of the photoelectron wavefunction is inclined at the scatterer. In other words, the peak does not shift from the forward direction but the forward direction has shifted already before the scattering.

This formula for the direction of the forward focusing peak is exact when the photoelectron wavefunction can be expressed by only one component of angular momentum. This condition is satisfied in the excitation of \( s \) core, where final \( m \) should be \( \pm 1 \). In the following, described is more general case of excitation.

The transition probability to the \( l' +1 \) final state is much higher than that to the \( l' -1 \) final state. In the case of the photoexcitation from the Si \( 2p \) \((l' =1) \) core state by a photon of \( \sigma_{h \nu} = +1 \), which is the case of ref \(^9\), the final \( l \) is either 2 or 0, and the final \((l, m) = (2, 2), (2, 1), (2, 0) \) and \((0, 0) \). The probability of realizing these three \( l=2 \) final states is much higher than that for \( l=0 \), and is about 13:1 at the photon energy of around 350 eV\(^{17}\).

The probabilities of realizing these three final \( m \) values are not equal because the Gaunt coefficients are different. For example, the probabilities for \((l, m) = (2, 2), (2, 1), (2, 0) \) are (6:3:1). When \( \sigma_{h \nu} = -1 \), the ratio for \( m=2, -1, 0 \) is also (6:3:1). Even when the spin-orbit interaction of the core state is considered, this ratio is unchanged for each spin-orbit split component \( p_{1/2} \) and \( p_{3/2} \). This ratio, however, is that of the total cross section over \( 4\pi \) steradian and it depends on the emission angle \( \theta \) (but does not depend on \( \phi \)).

The effective \( m \) value as a function of \( \theta, m^*(\theta) \), has been derived considering the spin-orbit interaction\(^{16}\). When the small contribution of \( l'=1 \) component is neglected, the \( m^*(\theta) \) for general \( l' \) initial state is expressed as
\[ m^*(\theta) = \frac{\sum_{l'=l}^{l'} \sum_{m'=l}^{m} \sum_{l'=l}^{l'} \sum_{m'=l}^{m} [c(l'+1, m, l', m')\Theta_{l'+1, m}]^2}{\sum_{m'=l}^{m} \sum_{l'=l}^{l'} \sum_{m'=l}^{m} [c(l'+1, m, l', m')\Theta_{l'+1, m}]^2} \]  
where \( m=m'+1 \) for \( \sigma_{h \nu} = +1 \). More general formula is written in\(^{16}\).

5. Stereoscopic photographs

A stereoscopic photograph consists of a pair of photographs; one is that to be seen by the left eye, and the other is to be seen by the right eye. The positions of an identical object in the two photographs differ by an amount of parallax, which is inversely proportional to the distance from the observer. Assume that you are facing the \( x \) direction and looking at an object A with your right and left eyes at E and F, respectively, as shown in Fig. 6. When the position of the object A is described as \((R, \theta, 0) \) in polar coordinates, the relation between the distance \( R \) and the azimuthal shift \( \Delta \) of the object A in the two photographs is described as
\[ \Delta = \tan^{-1} \left( \frac{\frac{b}{R \sin \theta}}{R \sin \theta} \right) \]  
where \( b \) is one half of the distance between the two eyes (OE and OF in Fig. 6).

6. Stereo photograph of atomic arrangement

Two photographs of atomic arrangement satisfying the condition of Eq. (6) can be obtained by using a display-type spherical-mirror analyzer described above in the measurement of circular dichroism in 2DAD. The first demonstration of stereo photograph was shown by the 2DAD pattern of W 4f photoelectrons from the W(110) surface at a kinetic energy of 800 eV by Daimon et al.\(^{18}\). Here we show a new result of stereograph on fcc Cu(001) surface, which is a common substrate of magnetic thin films. The stereo photograph for Fe overlayer was also obtained, and they showed clear fct structure. They will be presented elsewhere.

Fig. 7 (a) and (b) are the stereo photograph created with Cu 2p\(3/2\) photoelectrons taken with cw and ccw circularly polarized light, respectively. The photon energy was 1200 eV, and the kinetic energy of the photoelectron was 262 eV. These patterns are observed on a flat screen of the analyzer. The angular range on the screen is about \( \pm 60^\circ \).

The center of the figure nearly corresponds to the
Fig. 7 Stereo photographs of Cu crystal, which is photoelectron angular distribution pattern taken with clockwise (cw) circularly polarized-light (a), and counter cw light (b). By viewing (a) with the left eye and (b) with the right eye, we can image a three-dimensional fcc arrangement of atoms in Cu(001) crystal as shown in Fig. 8(b).

surface normal direction, which is the [001] axis. The ccw and cw excitation light is incident 45° inclined to the surface normal, as shown in Fig. 8(a). We can see six forward focusing peaks, such as A and B in the directions shown in Fig. 8. These forward peaks are produced by nearest neighbor atoms A and B shown in Fig. 8(a). Their positions in Fig. 7(a), (b) are, however, slightly different from the expected directions shown in Fig. 8(b). The peak positions in these two patterns are slightly shifted in a horizontal direction. For example, the peak A is slightly right in (a) and left in (b).

Because in both cases (Eqs. (1) and (6)) the angular shift $\Delta$ of the object is inversely proportional to the interatomic distance $R$ from the emitter, these patterns can be considered as stereoscopic photographs. Then, if we view the clockwise (cw) circularly polarized-light photoelectron angular distribution pattern (Fig. 7(a)) with the left eye and the ccw pattern (Fig. 7(b)) with the right eye, we can image a three-dimensional fcc arrangement of atoms in Cu(001) crystal as shown in Fig. 8(b). The A atom looks closer, and the B atoms look farther. Moreover, near atom looks stronger and far atoms look weak as in the case of real view. The split of the peak B is due to the subsidence of forward focusing peak at low kinetic energies.

To recognize the three-dimensional arrangement properly, it is necessary that the field of vision of both images should be the same as that in the measurement. The solid angle of these pictures is about $\pm 60^\circ$ in the measurement whereas it is only $\pm 15^\circ$ when these pictures are viewed by using usual stereo-viewer. Special projection method, such as a combination of polarized light projection and polarized glasses for individual image, is necessary to realize the field of vision of $\pm 60^\circ$. If it is realized, the inter-atomic relation is to be proportional to the real relation.

When Eq. (1) and Eq. (6) are identical, there is no distortion. The necessary condition is that $m / (k \sin \theta)$ be constant in Eq. (1). For the objects in the x-y plane, there is no distortion because $m / (k \sin \theta)$ is constant. In this case, the magnification ratio is $bk/m$. When $b = 3$ cm, $k = 14$ Å$^{-1}$ (for the kinetic energy of 800 eV), and $m=4$, the magnification ratio is about $2 \times 10^{10}$, which is 2000 times higher than usual electron microscope. When $\theta$ is not $90^\circ$, the sine function in the denominator of Eq. (1) would make the atoms closer to the viewer. However, this distortion is hardly present in the actual case because the value $m$ in Eq. (1) is not constant, and the $\theta$ dependence of $m^*\theta$ of eq. (5) is close to $\sin^2\theta$.

In this method the forward focusing peaks should be clearly seen in 2DAD pattern. This restriction implies that the emitter atom must lie under the scatterer atoms and that the kinetic energy of the photoelectron should be above several hundred eV. The photoelectron diffraction and the multiple-scattering effect could modify the forward focusing peaks, but these effects are order of magnitude smaller than the forward peaks. The peak positions have been reproduced well so far not only for the adsorbate single-scattering case but also for the bulk multiple-scattering case when the forward focusing peaks are clearly seen. Hence, this analysis is applicable not...
only to the molecules adsorbed on surfaces but also to the crystalline substances.

7. Stereo Microscope

This stereoscopic photograph can be obtained directly on the screen of above mentioned display-type spherical-mirror analyzer without any computer-aided conversion process. Rotatable analyzer method to measure photoelectrons two-dimensionally can also take this stereoscopic photograph with the aid of computer. However, rotating-sample method produces much-distorted image. Other types of display analyzers such as Eastman-type analyzer\(^7\)\(^,\)\(^8\) can also be used to take stereoscopic photographs. In this case, however, the pattern obtained on the screen is distorted, and computer processing is inevitably necessary to make the photograph.

Because only the display-type spherical-mirror analyzer can obtain a distortion-free image in much wider solid angles than the Eastman-type one, it is the best analyzer to take the stereoscopic photographs.

The image obtained by this stereo microscopy is the view from specific atoms selected by kinetic energy of photoelectrons. When the sample has many atoms, which have core states of the same binding energy, the image is the overlap of images from all those atoms inside the area irradiated by x-ray. This feature is similar to x-ray diffraction method. However, note that this method doesn't need periodic array. If there is a defect or an adatom that has cores with different binding energies, the structure around that atom can be viewed in principle.

Real-time observation will help understanding the dynamics of atoms. The problem in all atomic-structure analysis methods so far (electron diffraction, X-ray diffraction, photoelectron diffraction and holography) is that the data obtained are that of reciprocal space, and a real-space structure cannot be imaged before conversion. It takes some time to calculate the atomic structure, and these methods are thus not suitable for real-time analysis. The situation is even worse for fluorescent X-ray holography\(^19\) because the time for data collection is much longer than that for electron emission holography.

When the time required to switch the helicity of circularly polarized light is reduced and the signal intensity increases, this display analyzer will give an opportunity for real-time stereoscopic observation. On the screen of DIANA the stereoscopic photographs for right eye and left eye will be displayed alternately by switching the helicity of circularly polarized light. An alternate glasses can transmit each image to each eye by switching the transmittance of each glass with the same period. In this way one can image three-dimensional atomic arrangement as shown in Fig. 9 in real time.

References


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