Direct Imaging of Atomic Arrangement by Photoelectron Holography*

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The developments of photoelectron holography, which can display atomic arrangement directly without complicated calculation, are described mainly focusing on its early stage. Several analysis methods for photoelectron holography have been described with applications to Si(001) and W(110)(1×1)-O surfaces. The Small Window method combined with the Energy Summation method reconstructed atomic arrangement within a unit cell in reasonable accuracy. However the accuracy remains about 0.3 Å, and is not good as electron or x-ray diffraction methods, and the reconstructed region is limited to nearest or second nearest atoms. The main difficulty in photoelectron diffraction comes from strong forward focusing peaks. Recent development of many analysis methods in photoelectron holography has overcome this difficulty and has made Renaissance in this field.

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I. INTRODUCTION

Holography is a method to reproduce a three-dimensional structural image directly by using a hologram which is an interference pattern between the reference wave and an object wave. The so-called phase problem, which is a difficulty in x-ray diffraction analysis, does not exist in this method because the phase of the wave is memorized in a hologram, and a simple irradiation of a reference wave or a simple Fourier transformation can reproduce a three-dimensional structural image directly. Atomic resolution holography, however, has not been realized until recently because the coherency of the reference wave has not good enough to resolve atoms. The waves having enough coherencies for atomic-resolution can be realized by the wave emitted from one atom, such as photoelectrons from inner core state or fluorescent X-rays from an atom. Atomic resolution holographies using these atomic waves have been proposed in 1986 by Szöke [1] for photoelectron holography, and fluorescent x-ray holography was reported by Tegze in 1991 [2]. In these holographies, the waves emitted from a specific atom are used as a reference wave, and the waves scattered by nearby atoms are used as object waves. Because the emitter atom itself is a point source with a size of atom, a three-dimensional arrangement of atoms surrounding the emitter atom can be obtained in atomic resolution.

Although the idea of these atomic resolution holographies is simple the development of these techniques has not been straightforward. Many reconstruction methods have been proposed, but the accuracy of the reconstructed structure has not been as good as that of electron diffraction of x-ray diffraction methods. Recently, new methods have been developed and the photon flux of synchrotron radiation increased, and data acquisition technology also improved. These improvements realized the Renaissance of atomic resolution holography. Because the technique of photoelectron holography can analyze local atomic structure around specific atoms, such as dopant, which cannot be analyzed by usual x-ray diffraction technique, this Renaissance of photoelectron holography will contribute to effective development of new materials. Here the development of atomic resolution photoelectron holography is described.

II. FORMULAE OF PHOTOELECTRON HOLOGRAPHY

Figure 1 shows a schematic diagram of photoelectron diffraction and holography. An x-ray irradiates an emitter atom and produces a photoelectron. This photoelectron propagates as a wave (reference wave) \( \psi^0 \). Note that the angular distribution of its intensity and phase are not spherically symmetric but the wave front is spherical. The angular distribution of \( \psi^0 \) is calculated by a dipole transition from the initial state (usually inner core state) to the final (photoelectron) state. The variation of the intensity and the phase of \( \psi^0 \) is smooth. For example the angular distribution of photoelectron from s core is similar to \( p_x \) orbital where \( x \) direction is the direction of the electric vector of the incident x-ray.

The direct photoelectron wave \( \psi^0 \) is scattered by nearby atoms and produce a scattered wave \( \psi^S \). The angular distribution of the scattered wave \( \psi^S \) has a peak in a forward direction, which is called as a forward focusing peak, along the direction connecting the emitter and the scatterer atoms. The interference between the direct wave and the scattered wave produce diffraction rings around this forward focusing peak as shown in Fig. 1. The interference of many forward focusing peaks and diffraction rings from many scatterers produce a photoelectron diffraction pattern, which is considered as a hologram \( \chi(\mathbf{k}) \) where \( \mathbf{k} \) is the wave vector of the photoelectron.

The direct photoelectron wave (reference wave) \( \psi^0 \) outside the emitter atom in Fig. 1 is expressed as

\[ \psi^0 = A(\mathbf{k}) \exp(i\mathbf{k}r) / r \]  

(1)

Here \( A(\mathbf{k}) \) is a slowly varying complex function with respect to \( \mathbf{k} \) as mentioned above, and is neglected hereafter.

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The scattered wave from the \( j \)-th atom \( \psi_j^S \) can be expressed at the detector, which is sufficiently far from the atom, as

\[
\psi_j^S \rightarrow \frac{\exp(ikr)}{r} F_j(k) \exp(-i k \cdot r_j) \tag{2}
\]

where \( F_j(k) \) describes angular distribution (\( \hat{k} \) dependence) of the wave scattered by the \( j \)-th atom at \( r_j \), \( F_j(k) \) is expressed in single scattering approximation as

\[
F_j(k) = \frac{\exp(-ikr_j)}{r} f_j(k) \tag{3}
\]

where \( \frac{\exp(-ikr_j)}{r} \) denotes the propagation of \( \psi^0 \) to the scatterer atom and \( f_j(k) \) is a complex atomic scattering factor of the \( j \)-th atom for spherical direct wave \( \psi^0 \) at \( r_j \). When multiple scattering is considered \( F_j(k) \) describes an angular distribution for the sum of multiply scattered wave finally emits from the \( j \)-th atom. The photoelectron diffraction pattern function \( \chi(k) \) is the square of the sum of the direct photoelectron wave \( \psi^0 \) and the total scattering wave normalized by \( \psi^0 \) as

\[
\chi(k) = \left| \frac{\psi^0 + \sum_j \psi_j^S}{\psi^0} \right|^2 = 1 + \sum_j F_j(k) \exp(-i k \cdot r_j) \tag{4}
\]

The photoelectron diffraction pattern is the modulation of Eq. (4), hence we neglect the constant 1 and the square of the scattering wave, which is relatively small compared with that of \( \psi^0 \). Then \( \chi(k) \) can be expressed as

\[
\chi(k) \approx \sum_j \left\{ F_j^*(k) \exp(ik \cdot r_j) + F_j(k) \exp(-i k \cdot r_j) \right\} \tag{5}
\]

If we consider imaginary atom at \( -r_j \), which is located opposite to the scatterer atom at \( r_j \) with respect to the emitter atom, Eq. (5) can be written simply as

\[
\chi(k) \approx \sum_j F_j(k) \exp(-i k \cdot r_j) \tag{6}
\]

Hence the photoelectron diffraction pattern can be considered to be the Fourier transform of atomic arrangement if \( F_j^0(k) \) is constant.

In the method of photoelectron holography suggested by Barton [3] the holographic reconstruction of the atomic arrangement \( U(R) \) around the emitter is described by a simple two-dimensional Fourier transformation as

\[
U(R) = \left| \int \int_s \chi(k) \exp(i k \cdot R) d\mathbf{k} \right| \tag{7}
\]

where the integration is conducted on the sphere \( S \) of constant \( k \) in \( k \) space. Because Eq. (7) is a part of an inverse Fourier transformation of Eq. (6) the atomic arrangement will be reproduced at \( r_j \) and \( -r_j \). The atomic image at \( -r_j \) is called “twin image”. Because \( F_j(k) \) is not isotropic and has a phase, the accuracy of this holographic reconstruction image is not enough.

In order to obtain better holographic reconstructed image, several reconstruction techniques have been developed. Barton [4] removed multiple scattering effect and twin images by “Energy Summation (ES)” method, which sums several holograms of different kinetic energies, as

\[
U_{ES}(R) = \int d\mathbf{k} \exp(-i kr) \int \int_s \chi(k) \exp(i k \cdot R) d\mathbf{k} \tag{8}
\]

where the summation of the product of \( \exp(i k R) \) and \( \exp(ikr_j) \) enhances the intensity at \( r_j \) and depresses it at \( -r_j \). Eq. (8) is similar to the integration of Eq. (7) not only two-dimensionally but also in three-dimensionally in \( k \) space.

Toner et al. [5,6] developed “scattered wave included Fourier transform (SWIFT)”. This method divides \( \chi(k) \) by \( F_j(k) \) to remove its anisotropy. In this case we should know the atomic species at \( r_j \) before structure analysis, hence it is applicable only when the structure consists of single atomic species.

Tong et al. [7–9] developed “small window energy extension process (SWEEP)”. The small window method is expressed as,

\[
U_{SW}(R) = \int \int w(\alpha, R) \chi(k) \exp(-i k \cdot R) d\mathbf{k} \tag{9}
\]

where \( w \) is a window function which limits the integration in the region of solid angle \( \alpha \) around \( R \) direction. Using small window function \( w \), the effect of other atoms can be reduced because the anisotropy of \( F_j(k) \) is strong at the direction of individual scatterer atoms.

III. RECONSTRUCTION OF Si(001) SURFACE

These techniques have been applied to Si(001) surface [10]. Observed holograms (two-dimensional photoelectron diffraction patterns) are shown in Fig. 2. These data have been obtained by using a display-type spherical mirror analyzer [11,12] at Photon Factory.

The holographically reconstructed real space structural images using these data are shown in Fig. 3 and Fig. 4.
of 450 eV (Fig. 2 (b)). The images (a) and (d) are from the photoelectron diffraction pattern of the kinetic energy of (a) 350, (b) 450, and (c) 650 eV. The center corresponds to the surface normal direction and the peripheral of the circle corresponds to the polar angle of 47°. The horizontal direction is [110].

Figure 3 shows the images reconstructed only from the photoelectron diffraction pattern of the kinetic energy of 450 eV (Fig. 2 (b)). The images (a) and (d) are \( U(R) \) calculated by Eq. (7), and (b) and (e) are \( U^{SW}(R) \) calculated by Eq. (9). The white circles indicate the position of Si atoms expected from Si crystal structure shown in (c) and (f).

The peaks in the image of simple reconstruction \( U(R) \) consist of many stripes due to the effect of other atoms, and reconstructed atomic images are not clear. Several strong forward focusing peaks exist separately in the pattern produce high-frequency Fourier component, which corresponds to these stripes. These stripes have been removed in \( U^{SW}(R) \) using small window which removes strong forward focusing peaks arising from other atoms. Hence the peaks obtained in \( U^{SW}(R) \) are smoother than those obtained by the simple Fourier transformation. Because the integration is done in a constant \( k \)-sphere region the image is elongated vertically. Twin images are clearly seen at the bottom of Fig. 3(c).

IV. RECONSTRUCTION OF W(110)(1×1)-O SURFACE

The hologram (full-solid-angle x-ray photoelectron diffraction pattern) from W(110)(1×1)-O surface was used to test the resolution of photoelectron holography [13]. Measurement was done by using conventional x-ray source (Al Kα) and by rotating sample around two-axes by computer controlled motors [14]. The photoelectron diffraction pattern was measured for the polar angle range from \( \theta = 0^\circ \) to \( \theta = 81^\circ \) in steps of 3°, and over the 360° azimuthal angle range in steps of 2°.

Figure 5 shows the structure model of W(110) (1×1)-O surface viewed from [110] direction. Big and small circles indicate tungsten and adsorbate oxygen atoms, respectively.

Figures 6(a) and (b) show the full-solid-angle photoelectron diffraction pattern of the O 1s peak. The center of the pattern corresponds to the surface normal (\( \theta = 0^\circ \)) and the periphery corresponds to \( \theta = 81^\circ \). Figure 6(a) was made in stereo-projection method. In Fig. 6(b) the wave numbers \( k_x \) and \( k_y \) are linear in this plane. These patterns have been averaged utilizing the horizontal and vertical mirror symmetries considering the symmetry of W(110) crystal, i.e., with respect to the [001] and [110]
FIG. 5: Structure of W(110) (1×1)-O surface viewed from [110] direction. Big and small circles indicate tungsten and adsorbate oxygen atoms, respectively.

directions.

Figures 6(a) and (b) are typical photoelectron diffraction patterns from top layer atoms. In Fig. 6(a), we can find six double rings in the directions of the nearest neighbor oxygen atoms from the emitter ([001], [001], [111], [111], [111], [111]). In this case the axes of these diffraction rings should lie in the surface plane, which is confirmed by the fact that the double rings look as parallel pair of lines in Fig. 6(b). All of these ring-pairs are the first and second order diffraction rings originated from in-plane oxygen pairs in these directions, and the fact that they look as lines is a proof that the oxygen atoms exist in the outmost plane.

Figures 7(a) and (b) show the cross section of the holographic reconstructed images of the photoelectron diffraction pattern of Fig. 6 in the plane of adsorbed oxygen layer. The displayed area (x × y) of these planes is 15 Å×15 Å, which size is adequate considering the mean-free-path of the photoelectron emitted from O1s. White open circles show the positions of oxygen atoms expected from the lattice constant of tungsten substrate.

Figure 7(a) is obtained by the simple Fourier transformation $U(R)$ calculated by Eq. (7), and (b) is obtained by the Small Window method $U_{SW}(R)$ calculated by Eq. (9). In Fig. 7(a) we can notice that each bright spot consists of many stripes similar to those seen in Fig. 3, however, these stripes disappeared again in $U_{SW}(R)$ of Fig. 7(b). Therefore, we can conclude again that these stripes are caused by the contribution of other atoms.

Although the atomic positions obtained by the holographic reconstruction are in agreement with real structures, the peak positions in Fig. 7(b) are shifted outward by 0.9 Å (which is 29% of the interatomic distance of 3.16 Å) We discuss about this shift from the expected positions. We can guess three reasons for this shift: (1) the angular dependence of the atomic scattering factor has not been considered in these holographic reconstructions, (2) the effect of the multiple scattering has not been included, (3) the actual positions of oxygen atoms differ a little from the ideal (1×1) positions, which means that the overlayer is incommensurate.

In order to examine these candidates, we compared this holographic reconstructed image (Fig. 7(b)) with those obtained from calculated photoelectron diffraction patterns. To calculate photoelectron diffraction patterns, we have used the SCAT program package [15]. This program includes the multiple-scattering approach developed by Rehr and Albers [16], which was applied earlier to the photoelectron diffraction by Kaduwela, Friedman and Fadley [17].

Figure 8(a) shows the calculated photoelectron diffraction pattern emitted from an oxygen atom, taking only the first nearest-neighbor six scatterers into account, and Fig. 8(b) shows its holographic reconstructed image. It is clearly seen that the positions of bright spots in the holographic reconstructed image are in better agreement with the expected positions with an accuracy of 0.25 Å (8%). Because both the anisotropic atomic scattering factor and the effect of multiple scattering are included in the calculation, it is concluded that the large shift of the peak position in the observed holographic reconstructed image (shown in Fig. 7) is not caused by the ignorance of them.
and the candidates (1) and (2) are denied. It is interesting to think about the candidate (3), which means that the distance between the adsorbate atoms are larger than the lattice constant of the substrate. This model was once used to explain the superstructure spots of LEED [18,19] from this surface. Although these superstructure spots have been explained by domain structure from STM image [20], the stretching of lattice constant cannot be denied by STM.

V. RECENT PROGRESS OF PHOTOELECTRON HOLOGRAPHY

As described in the previous sections using the application to the measured holograms from Si(001) and W(110)(1×1)-O surfaces, the Small Window Energy Extension Process (SWEEP) method reproduces atomic arrangement in a reasonable accuracy without twin images. The discussion with the calculated diffraction pattern revealed that the ignorance of the anisotropy of atomic scattering factor or the effects of multiple scattering is not serious. However the accuracy remains about 0.3 Å, and is not good as electron or x-ray diffraction methods, and the reconstructed region is limited to nearest or second nearest atoms. The main difficulty in photoelectron diffraction comes from strong forward focusing peaks; its strong anisotropy hampers simple Fourier transformation and its phase produce the shift of the image. Some other methods have been developed to increase the accuracy. Differential holography was developed by...
Omori et al. [21], which uses the difference of holograms at different kinetic energies. Because the shape of forward focusing peaks weakly depends on the kinetic energy but the radius of diffraction rings strongly depends on the kinetic energy, strong forward focusing peaks disappear and only the diffraction rings remain in the difference pattern. Near node holography was developed by Greber and Osterwalder et al. [22, 23], which utilizes the phenomenon that the angular distribution of photoelectron excitation cross section has a node in direction perpendicular to the photon polarization direction when the initial state is core. The experimental geometry is chosen so that the detection direction is nearly perpendicular to the polarization of the incident photon. In this geometry, the strong forward focusing peak is not observed and the diffraction rings are enhanced. Therefore, the accuracy of the analysis increases.

Very recently a new method of photoelectron holography called SPEA-MEM was developed by Matsushita et al. [24-27]. SPEA-MEM is the reconstruction algorithm, scattering pattern extraction algorithm (SPEA) with maximum entropy method (MEM). Although it does not use a Fourier transformation, it can analyze the hologram directly without assumption. One hundred atoms could be resolved using one kinetic energy hologram. This method has been applied to other holographies such as x-ray fluorescence holography.

More direct method of Stereophotography of atomic arrangement has been developed by Daimon [28] recently. The photoelectron diffraction patterns excited by left- and right-hand circularly polarized x-rays are found to be stereographs for left and right eyes, respectively. Hence one can view the atomic arrangement directly in three-dimensionally by naked eyes.

Because these techniques of photoelectron holography are element selective, and the modulation of intensity is much stronger than x-ray fluorescence holography, this Renaissance of photoelectron holography will be widely used to analyze and develop new materials.

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