"Negative photographic film"-like diffraction phenomenon found in photoelectron energy loss process

Photoelectron diffraction (PD) is an element-selective local structure analysis method. Atomic arrangements around photoelectron emitter atoms are deduced from the directions of forward focusing peaks (FFPs) and the diffraction rings around them. Recently, a direct atomic arrangement reconstruction algorithm from PD patterns has been developed, and the quality of reconstructed images has been significantly improved [1]. Furthermore, FFPs from inequivalent sites appear in different directions, so the position of a photoelectron emitter atom can be specified. PD combined with a spectroscopic method enables the investigation of the local-atomic-site-specific electronic properties [2].

However most emitted electrons undergo energy loss process. Indeed, energy dissipation is a ubiquitous phenomenon. PD patterns are destroyed by inelastic scattering. There were pioneering works on PD by Osterwalder and coworkers [3,4]. However energy-loss electrons were treated as mere obstacles that disturb photoelectron spectral measurement. We investigated this phenomenon in detail and found that completely reversed contrast patterns of the original PD appeared in the energy loss electron angular distribution [5]. This contrast reversal becomes dominant over PD pattern destruction with an energy loss larger than 80 eV. The mechanism of this new phenomenon is explained by the decrease in energy-loss electron intensity caused by absorption through inverse PD process just like a negative photographic film.

All the experiments were carried out using the two-dimensional display-type analyzer installed at the circularly polarized soft X-ray beamline **BL25SU**. Figures 1(a)-1(d) show the set of 2π-steradian Ge 3*p* PD patterns from the Ge(111) surface with photoelectron kinetic energies of 400, 600, 800, and 1000 eV, respectively. PD patterns obtained by both helicity excitations are summed. The positions of highly symmetric directions are indicated in Fig. 1(a). The dotted lines and dashed curves in Fig. 1(d) indicate the $\{1\bar{1}0\}$ and $\{110\}$ planes, respectively.

Three kinds of bright FFPs were observed in the $\langle 11\bar{1}\rangle$, $\langle 110\rangle$, and $\langle 001\rangle$ directions in Ge 3*p* PD patterns. They correspond to the directions of the first-, second-, and fourth-nearest Ge atoms, respectively. Diffraction patterns change markedly as the kinetic energy varies. Blue lines in Fig. 1(d) indicate the diffraction rings around FFPs. Their radii decrease as the kinetic energy increases.

Figures 1(e)-1(g) show a series of 2π-steradian energy-loss electron patterns at a kinetic energy of 600 eV. The photon energy was varied so that the kinetic energy is set to 40, 80, and 160 eV off the Ge 3*p* elastic peak. We found that the PD patterns are destroyed at 40 eV off the elastic peak, as discussed previously [3]. In Figs. 1(f) and 1(g), dark regions appear at the position of FFPs in Figs. 1(a)-1(d). Figure 1(h) is a contrast-reversed presentation of Fig. 1(g), which is almost a complete negative replica of PD in Fig. 1(b). The diffraction rings and Kikuchi-band-like features are identical. A negative 600-eV PD replica was observed in the energy-loss electron pattern from 160 eV and even at 350 eV off the elastic peak. The kinetic energy of the original elastic peak is much larger than those of energy-loss

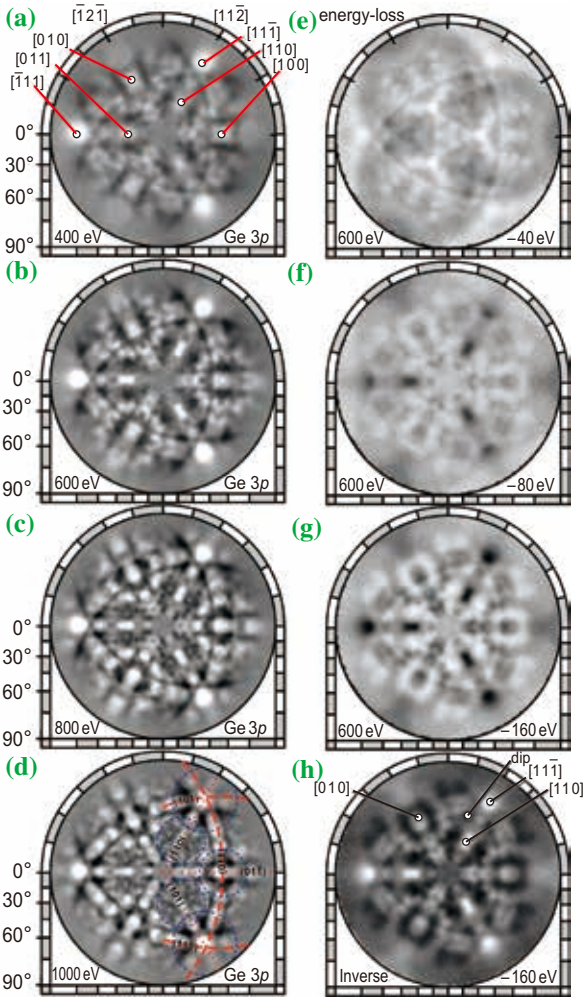

Fig. 1. **(a)-(d)** 2π-steradian Ge 3*p* photoelectron diffraction patterns at kinetic energies of 400–1000 eV. **(e)-(g)** 2π-steradian energy-loss electron patterns at a kinetic energy of 600 eV. Photon energy was varied. **(h)** is a contrast reversed presentation of (g).

electron patterns with the same kinetic energy of 600 eV in Fig. 1(b), but not that with higher or lower kinetic energies. The defocusing effect induced by inelastic plasmon excitation and electron blocking by atomic chains [4] cannot explain the appearance of this same negative replica pattern in the energy-loss electron patterns with different photon energy excitations.

Figure 2 shows a summary of the photon energy dependence of the diffraction and circular dichroism contrasts. The abscissa is the binding energy relative to the Ge 3*p* core level. PD contrasts above and below unity correspond to the constructive and destructive interferences, respectively. Note that the FFP intensities in the [11$\bar{1}$] and [001] directions rapidly decrease as the binding energy increases and then become smaller than unity at 80 eV off the Ge 3*p* elastic peak. The contrast becomes nearly constant at an energy beyond 120 eV. On the other hand, the contrasts of the dips around [11$\bar{1}$] FFPs are below unity, but as the binding energy increases they become larger than unity. The photoelectron spectrum is also shown. Ge 3*p* and 3*s* photoelectron peaks appeared at 0 and 58 eV, respectively. Ticks indicate a series of plasmon loss peaks at an interval of 16 eV. The shoulder structures observed in the diffraction and circular dichroism contrasts at 40 eV are due to Ge 3*s* core level excitation.

Figure 3(a) illustrates the models of normal PD. The dotted arc indicates the position of a display-type detector. PD is the interference of direct waves from a photoelectron emitter atom and of scattered waves generated by the surrounding atoms. As shown in the model, intense FFPs are observed in the direction of the surrounding atoms.

On the other hand, the mechanism of this new phenomenon can be qualitatively explained by the decrease in isotropic energy-loss electron beam intensity caused by absorption process. Figure 3(b) shows an electron wave undergoing scattering and being absorbed by the emitter atom. The proposed model shown in Fig. 3(c) is the absorption process. This absorption process takes place at every atomic site in the crystal. Electrons are partially absorbed, some of which are emitted in vacuum. As a result, dark low-transmission patterns appear.

The circular dichroism pattern observed in the original PD disappeared in the negative replica PD pattern. A similar phenomenon has been observed in electron backscatter diffraction. Therefore, this phenomenon is independent of the excitation source and its polarization. A new method of atomic structure analysis based on this *negative-photographic-film-like* diffraction phenomenon is expected to be realized.

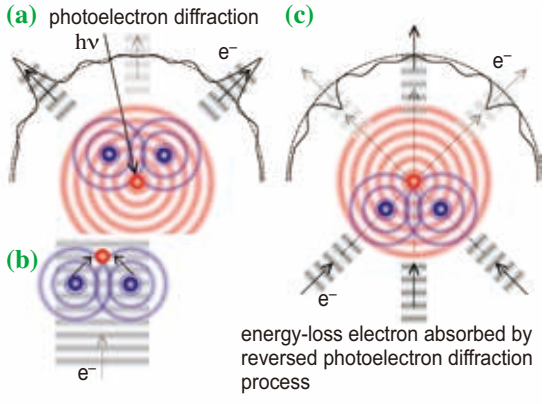

Fig. 3. Schematic illustrations of the mechanisms of **(a)** normal PD, **(b)** electron absorption process, and **(c)** time- and space-reversed PD process. Solid lines indicate the emitted electron intensity.

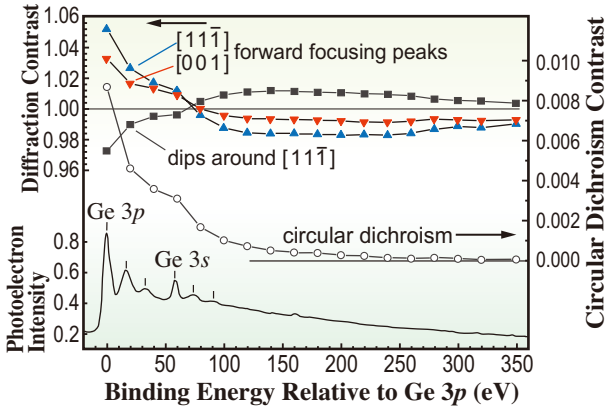

Fig. 2. Energy dependence of FFPs, destructive interference patterns, and circular dichroism contrasts together with photoelectron spectrum.

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