Three-dimensional band mapping of graphite

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We developed a method to visualize the curved surfaces of valence band dispersion by a display-type spherical mirror analyzer. The $\pi$ and $\sigma$ band “surfaces” of graphite measured and displayed three dimensionally contain fruitful information compared to the conventional band dispersion “curves” along a certain direction in $k$ space. The slope and the curvature of local band structure correspond to the velocity and the mass of the valence electrons. By integrating band energy over the entire Brillouin zone, the electronic part of the condensation energy is obtained. Furthermore, the atomic orbitals composing each band are determined from two-dimensional photoelectron intensity distribution by using linearly polarized synchrotron radiation. © 2002 American Institute of Physics. [DOI: 10.1063/1.1511181]

As a direct probe for the valence electrons, angle-resolved photoelectron spectroscopy (ARPES) has been an indispensable tool for elucidating the electronic nature of various solids. ARPES gives the most detailed information about the band structure $E_g(k)$ resolved in binding energy $E_B$ and wave vector $k$. However, investigations of ARPES, so far have been concentrated in a certain two-dimensional cross section of the valence band structure, i.e., two-dimensional band dispersion $E_g(k_x)$ or isoenergetic line shapes such as a cross section of Fermi surface, $E_F(k_x,k_y)$. Here we present the three-dimensional [E_B $-k_x-k_y$] dispersions of the $\pi$ and $\sigma$ bands of the single-crystalline graphite by using a two-dimensional display-type spherical mirror analyzer (DIANA). Furthermore, the atomic orbitals composing each band have been determined by analyzing the two-dimensional photoelectron angular distribution (PEAD) excited by a linearly polarized synchrotron radiation (SR).

Figure 1 is a schematic cross section of DIANA used for the measurement of two-dimensional PEAD patterns. Linearly polarized SR is introduced through a hole in the obstacle rings. A spherical electric field applied between the obstacle rings and the main grid focuses photoelectrons with a selected kinetic energy on to the aperture. These photoelectrons are multiplied by microchannel plate (MCP) and projected to a fluorescent screen with the emission angle preserved. Thus the momentum of the photoelectrons parallel to the surface can be deduced directly from the position of the PEAD pattern on the screen. The energy resolution of this analyzer $\Delta E/E$ is 1% and the angular resolution is $1^\circ$, which are 350 meV and 0.06 Å$^{-1}$ at 35 eV. The experiment was performed at the linearly polarized soft x-ray beam-line BL-7 of Ritsumeikan SR Center in Shiga, Japan. The range of photon energy $(h\nu)$ covered by a modified Rowland mount spherical grating monochromator is 35–130 eV. A synthetic graphite single crystal was used for the experiment. The method of sample preparation was described elsewhere. The sample was oriented so that one of the shortest C–C bonds (1–M direction) lies horizontally, which is along the electric vector of the normal incident SR. Typical acquisition time for one PEAD measurement was 5 min.

The graphite $\pi$ band has a parabolic dispersion with its bottom at the $\Gamma$ point and maxima at the six $K$ points. The PEAD patterns shown in Figs. 2(a)–2(d) correspond to the cross section of the $\pi$ band at the binding energy of 0.0, 1.0, 2.0, and 3.0 eV from the Fermi level, respectively. A photon energy of 52.5 eV, where the intensity of umklapp process is found to be considerably reduced, is chosen for the excitation. White hexagons indicate the first Brillouin zone (BZ) of graphite. All the PEAD patterns show twofold symmetry due to the linear polarization of the incident light. For instance, at the Fermi level [Fig. 2(a)], bright spots appear at the four left

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FIG. 1. Schematic cross section of a display-type spherical mirror analyzer.
The periphery corresponds to the acceptance angle of the analyzer, which is ± 50° from the surface normal. The BZ boundaries in Figs. 2(e)–(g) are for the photoelectron of the kinetic energy $E_k = 48$ eV. In the case of the $2p_z$ orbital, the photoemission intensity is high along the central vertical line. On the contrary, the same line is forbidden for the case of $2p_{x,y}$-orbital. The photoemissions from $2p_{x,y}$ and $2p_z$-orbitals can be distinguished by rotating the azimuthal angle of the sample by 90°.5 Photoemission intensity from the K points along the horizontal line is observed indicating that the $\pi$ band consists of mainly C $2p_z$ atomic orbitals.

The band dispersion is extracted by (1) stacking a series of PEAD patterns of different binding energies, (2) making energy distribution curves (EDC) at all $(k_x, k_y)$ pixels, and (3) determining the peak energy $E_B$ in each EDC. The PSF and the uneven detection efficiency of analyzer, which affect the intensity of EDC, do not alter the final band dispersion. The PEAD patterns for binding energies from −1.0 to 10.0 eV are taken with intervals of 0.2 eV. Data were averaged assuming horizontal and vertical mirror symmetry. Figure 2(h) is the bird’s-eye-view stereograph of the extracted three-dimensional band dispersion surfaces. The bright areas are where the original photoemission intensity is high. The first BZ of the graphite is indicated as a green hexagonal prism with one-fourth of its volume cut away to indicate the $\Gamma − K$ and $\Gamma − M$ direction. The top of the prism corresponds to the Fermi level and the bottom to the binding energy of 10 eV.

The patches of the hexagonal tiles underneath stand for the other BZs. The three-dimensional shape of the $\pi$ band dispersion such as the saddle-like feature at the M points or vertices at K points is easily recognized. The $\sigma$ band dispersion colored yellow has a maximum at the $\Gamma$ point and saddle-like feature at the M points.

Figures 2(i) and 2(j) are the top views of the $\pi$ and $\sigma$ bands, respectively, which are two-dimensional distributions of photoemission intensity (excitation probabilities) of these bands. The vertex and center of the hexagonal BZ tiles correspond to K and $\Gamma$ points, respectively. The photoemission intensity of the $\pi$ band is high at left- and right-hand sides, which corresponds to the simulated angular distribution pattern from a $2p_z$ atomic orbital as shown in Fig. 2(g). However, the fine structure of photoelectron intensity found around $\Gamma$ point does not agree with this simulation. This suggests the hybridization with atomic orbitals other than $2p_z$ around $\Gamma$ point. The energy of the $\pi$ band averaged all over the BZ is 3.93 eV. The difference of this value and that of the initial $\pi$ atomic orbital gives the electronic contribution of $\pi$ band to the formation energy of graphite. Although the precise value will be obtained only after all $k_z$ measurement, this kind of information can only be obtained by three-dimensional measurement of band structure.

On the other hand, the $\sigma$ band shows no photoemission intensity along the horizontal direction. Its maximum intensity appears along the four upper and lower $\Gamma − M$ directions. These trends also appeared in the simulated angular distribution pattern from a $2p_x$ atomic orbital in Fig. 2(f). However, the simulation indicates that the photoemission from $2p_x$ is forbidden along vertical and horizontal lines. The intensity observed at this area of the $\sigma$ band in Fig. 2(j) can be attrib-
FIG. 3. Motion of electrons in $\pi$ band. The length, position, and direction indicate the group velocity, wave vector $k$, and direction of electrons. The BZ is indicated by a hexagon.

uted to the contribution from the overlapping C $2p_z$ orbital.

Figure 3 depicts the motion of electrons in the $\pi$ band. Arrows indicate group velocity and direction for every momentum $k$ obtained by differentiating the curved $\pi$ band surface $dE/\partial k$. Note that arrows point radially around $\Gamma$ point but focuses to $K$ point at edge of BZ.

To conclude, the visualization of the curved surfaces of the graphite valence band is presented by the use of DIANA and linearly polarized SR. The two-dimensional ARPES measurement is demonstrated to show its ability in the exploration of the valence band structure in complete BZ. These band dispersion "surfaces" contain fruitful information compared to the conventional band dispersion "curves" along a certain direction in $k$ space. For instance, the atomic orbitals composing each band can be determined from two-dimensional photoelectron intensity distribution. The angular dependence of the slope (the velocity) and the curvature (the mass) of local band structure can be derived. The integrated band energy over entire BZ, which can be thought of as the electronic part of the condensation energy could also be obtained.

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