Atomic-orbital analysis of the Cu(111) surface state by two-dimensional photoelectron spectroscopy with linearly polarized synchrotron radiation

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Abstract

We have performed two-dimensional photoelectron spectroscopy measurements on Cu(111) surface. A two-dimensional photoelectron intensity angular distribution (PIAD) from the Cu(111) surface was obtained using a display-type analyzer and linearly polarized synchrotron radiation. With the grazing incident geometry, we have successfully obtained the PIAD from the Cu(111) Shockley surface state. However, its PIAD was highly asymmetric. This suggests that the Cu(111) Shockley surface state is composed of *s* orbital and/or *p*, *d* orbital normal to the surface.

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1. Introduction

The Cu(111) Shockley surface state has attracted much attention due to its fundamental physical properties, such as two dimensional nearly free electron like behavior and electron phonon coupling [1]. The Cu(111) Shockley surface state appears in the L-gap of the projected bulk band structure. The Cu(111) Shockley surface state has a circular Fermi surface (FS) and a parabolic band dispersion with the band bottom energy of ε_0 ~ -0.4 V, the effective band mass of m^*/m_e ~ 0.4, and the Fermi wave number of k_F ~ 0.2 $Å^{-1}$ [1]. By utilizing a high-resolution angle-resolved photoelectron spectroscopy (ARPES), some physical properties such as the life time of electron have been obtained [1]. For further investigation of the physical properties, knowledge about the atomic orbitals constituting the surface state would be desirable.

Photoelectron spectroscopy (PES) measurements excited with linearly polarized photon are very useful to determine the symmetry of the atomic orbitals constituting the electronic state. So far, the symmetry of the atomic orbitals has been analyzed by comparing photoelectron intensity along several symmetry lines. In this method, only even or odd symmetry with respect to the measuring plane can be determined. On the other hand, from a two-dimensional photoelectron intensity angular distribution (PIAD) obtained by using a polarized synchrotron radiation (SR) and a two-dimensional display-type spherical mirror analyzer (DIANA) [2], one can analyze the component ratio among atomic orbitals [3]. For example, two-dimensional PES (2D-PES) measurements on Cu with linearly polarized SR have revealed that the FS of Cu is composed of mainly 4*p* orbitals with their axes pointing outward [4]. In this work, we have performed 2D-PES measurements on Cu(111) surface taken with linearly polarized SR in order to determine the atomic orbitals constituting the Cu(111) Shockley surface state.

2. Experiment

2D-PES measurements were performed at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University [5]. The electric vector of the linearly polarized SR light was in the horizontal plane. The Cu(111) single crystal sample was cleaned by repeated cycles of Ar^+ bombardment and annealing to 500 ^oC. The surface quality was checked by low energy electron diffraction and Auger electron spectroscopy. The 2D-PES measurements were performed at room temperature under ultrahigh vacuum of $\sim 1\times 10^{-8}$ Pa using DIANA [2, 6]. Two-dimensional PIAD is efficiently obtained by using DIANA. The PIAD of this experiment was collected by energy window of 100 meV. Typical acquisition time for one PIAD was 30 sec for Cu

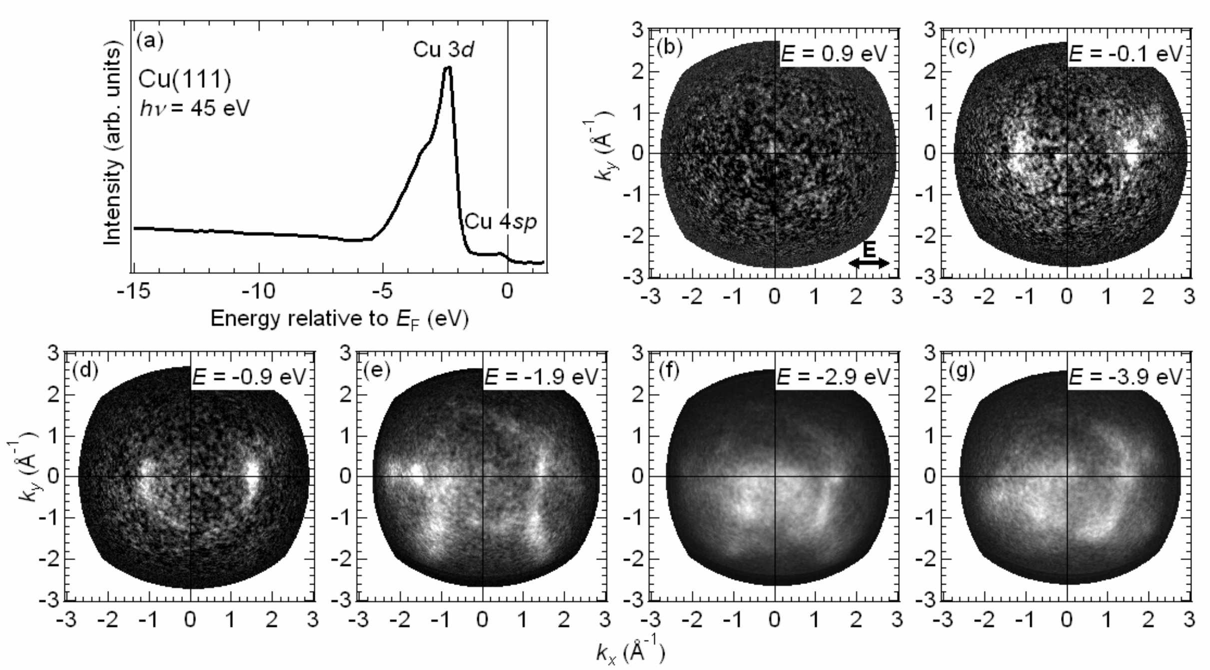

Fig. 1 2D-PES results of Cu(111) taken with $h\nu$ = 45 eV. (a) Angle-integrated PES spectrum. The PIADs at E = 0.9 eV (b), -0.1 eV (c), -0.9 eV (d), -1.9 eV (e), -2.9 eV (f), and -3.9 eV (g). The electric vector of the incident light is in the horizontal direction.

bulk band and 180 sec for the Cu(111) Shockley surface state. The total energy resolution was about 200-400 meV depending on the photon energy. The angular resolution was about 1°.

3. Results

Figure 1 (a) shows the angle-integrated spectrum of Cu(111) taken with $h\nu$ = 45 eV. The bands near the Fermi level are mainly composed of Cu 4*sp* states while those between -5 and -2 eV belong mainly to Cu 3*d* states. The contamination peaks around -6 and -10 eV were very weak, also confirming the sample surface cleanness. As shown in Fig. 1, the series of PIAD at various energies clearly show the dispersion of the Cu band structure. However, the symmetry of the PIAD pattern was different from the expected one with a three-fold symmetry due to the face-centered-cubic (fcc) crystal structure of Cu. This is due to the matrix element effect of the incident linearly polarized SR light. By rotating the sample around the (111) surface normal, the angle-dependent PIADs were obtained. As shown in Fig. 2, the PIADs both near the Fermi level and Cu 3*d* band rotate clockwise with increasing the angle ϕ and coincide with those rotated by 120°. This indicates that the measured band structure indeed have

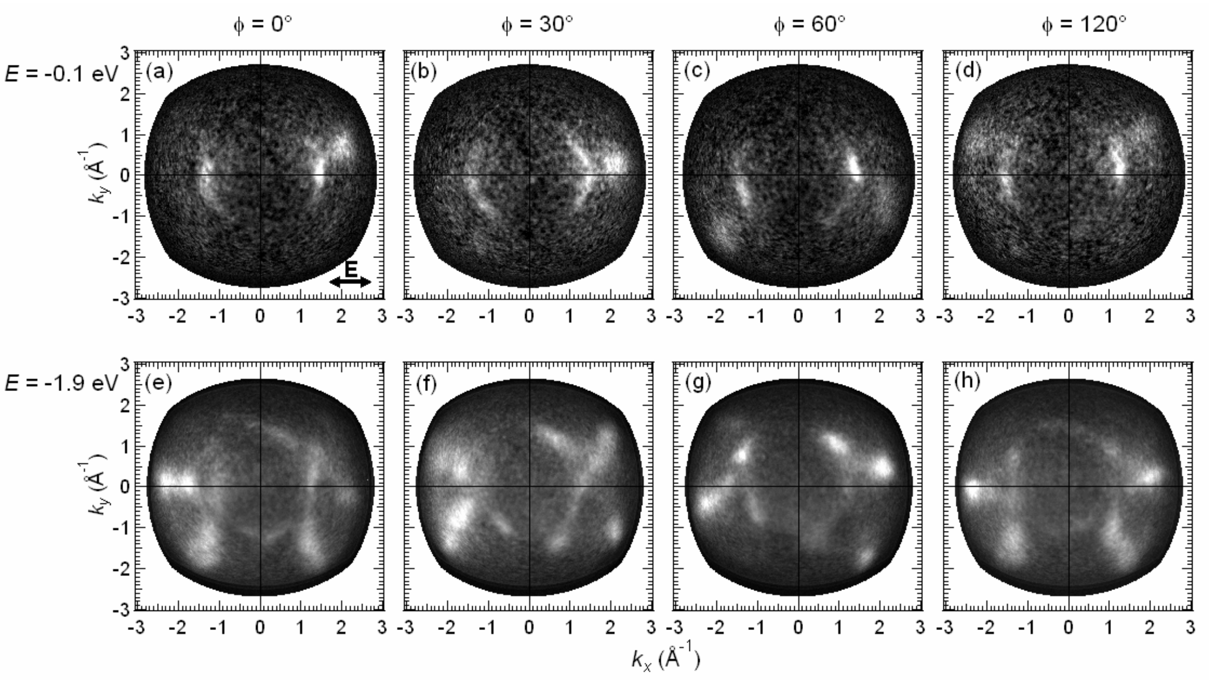

Fig. 2 Angle-dependent PIADs near Fermi level (E = -0.1 eV) and Cu 3d band (E = -1.9 eV) taken with $h\nu$ = 45 eV. The PIADs of ϕ = 0^o (a, e), 30^o (b, f), 60^o (c, g), and 120^o (d, h) near Fermi level and Cu 3d band.

a three-fold symmetry due to the fcc crystal structure of Cu. From these results, we concluded that the Cu bulk band structure was successfully obtained. Nevertheless, the Cu(111) Shockley surface state, which should appear around the center, was not observed. This is due to the matrix element effect by the polarization of the excited light since these 2D-PES measurements were performed with the normal incident geometry, i.e., the forbidden *s*-polarized geometry [7].

Thus, we have performed 2D-PES measurements with the grazing incident geometry. The incident angle with respect to the sample surface normal was set to 30°. The PIADs taken with the photon energy of 22.5 eV are shown in Fig. 3. As in the case of previous ARPES results taken with He I source ($h\nu$ = 21.2 eV) [1], both the FS of the Cu bulk band in the outside region ($|\mathbf{k}|$ ~ 1.5 Å^{-1}) and the Cu(111) Shockley surface state at the center were successfully observed [Fig. 3(b)]. With decreasing the energy, both the Cu bulk band and the Cu(111) Shockley surface state clearly show the dispersion as shown in Fig. 3. The Cu(111) Shockley surface state disappeared below ~ -0.4 eV [see Fig. 3(d) and (e)]. This observation is consistent with the fact that the bottom of the Cu(111) Shockley surface state band is located at ~ -0.4 eV [1].

In order to further investigate the Cu(111) Shockley surface state, we have performed 2D-PES measurements with decreasing the photon energy to 13.5 eV (Fig. 4).

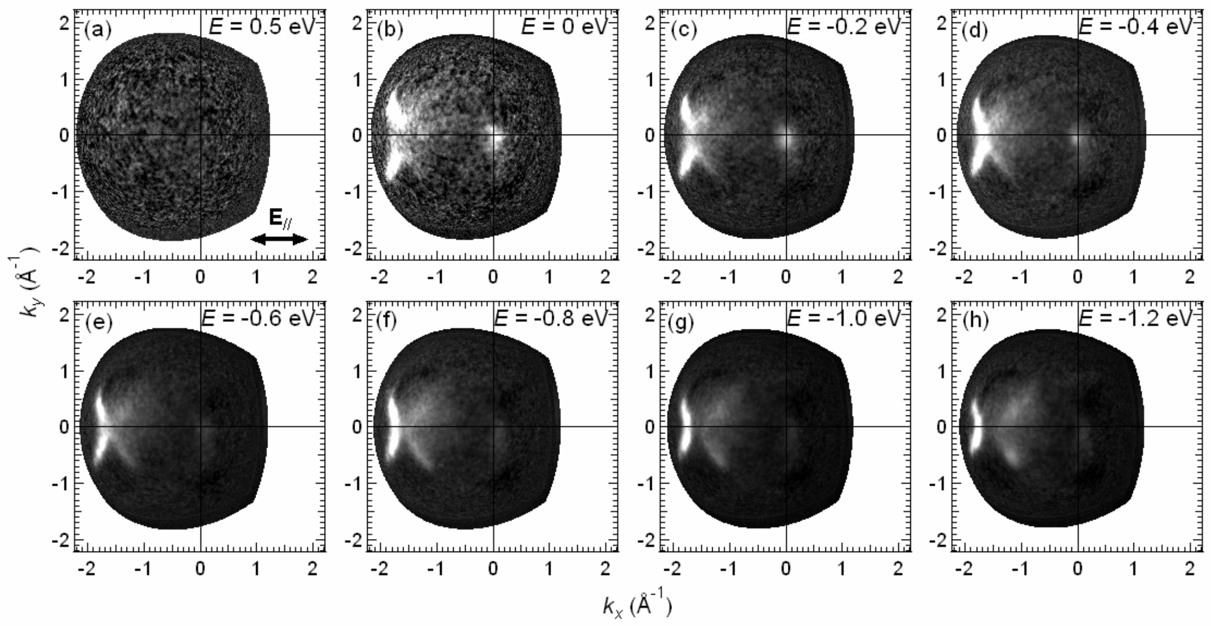

Fig. 3 2D-PES results of Cu(111) with grazing incident geometry taken with $h\nu$ = 22.5 eV. The PIADs at E = 0.5 eV (a), 0 eV (b), -0.2 eV (c), -0.4 eV (d), -0.6 eV (e), -0.8 eV (f), -1.0 eV (g), -1.2 eV (h), -1.4 eV (i). The surface parallel component of the electric vector of the incident light is in the horizontal direction.

According to the previous work [1], the FS of the Cu(111) Shockley surface state appears as a circle with the radius of ~ 0.2 Å^{-1}. The obtained PIADs of FS seem to have the same circular FS (dashed circle in Fig. 4). However, its photoelectron intensity was highly asymmetric, i.e., the photoelectron intensity in the right hand side region of the circular FS was strong [1, 7]. By rotating the sample around the (111) surface normal, we have found that the photoelectron intensity in the right hand side region of the

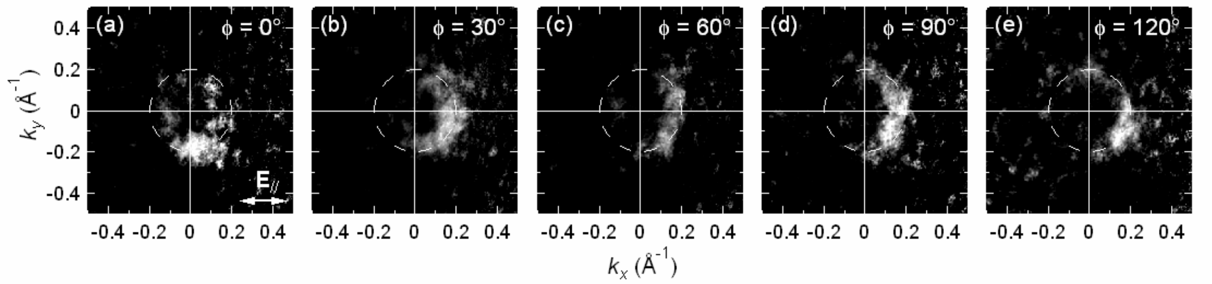

Fig. 4 PIADs of the FS for the Cu(111) Shockley surface state taken with $h\nu$ = 13.5 eV. The PIADs with various angles of $\phi = 0^{\circ}$ (a), 30° (b), 60° (c), 90° (d), and 120° (e) were obtained by rotating the sample around (111) surface normal. The dashed circle with the radius of ~ 0.2 Å^{-1} is also shown. The surface parallel component of the electric vector of the incident light is in the horizontal direction.

circular FS was always strong as shown in Fig. 4. This is due to the relation between the polarization vector of the incident SR and the atomic orbitals constituting the Cu(111) Shockley surface state.

4. Discussion

The analysis of two-dimensional PIAD from a tight-binding approximated valence band and a Bloch-wave final state showed that the photoelectron intensity $I(\theta, \phi)$ in the direction of polar angle θ and azimuth angle ϕ can be expressed as[4, 8]:

$$I(\theta, \phi) \sim D^1(k_{//})\ |\Sigma_\nu A_\nu|^2,$$

where $D^1(k_{//})$ is the one-dimensional density of states [9] and A_ν is the "angular distribution from the ν–th atomic orbital" [10]. The calculated $|A_\nu|^2$ from some fundamental atomic orbitals are shown in Fig. 5. As in the experimental condition, the linearly polarized SR ($\boldsymbol{E}_{//}$ // x) is incident from -x direction with the angle 30° from z axis. Here, we set the [111] direction to z axis. As shown in Fig. 5, the angular distribution from an atomic orbital is not uniform but unique to the atomic orbital due to the relation between the polarization vector of the incident SR and the atomic orbital. Therefore, comparing the experimental PIAD with these angular distributions from the atomic orbitals, one can determined the atomic orbitals constituting the electronic state. Rotated around z axis ([111] direction), the atomic orbitals which always have a strong angular distribution in the right hand side region are s orbital, p_z orbital, and $d_{3z^2-r^2}$ orbital. Assuming that the Cu(111) Shockley surface state has a circular FS with the radius of 0.2 Å^{-1} [1] and the work function is 4.7 eV [4], the PIAD taken with $h\nu$ = 13.5 eV for each atomic orbital is simulated as shown in Fig. 6. The simulated PIADs

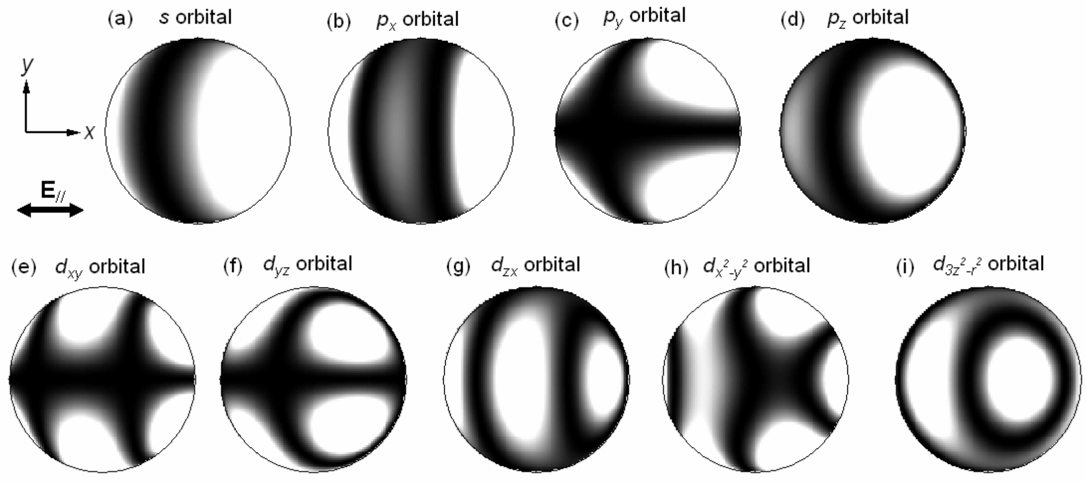

Fig. 5 Calculated angular distributions from some fundamental atomic orbitals [10]. (a) s orbital. (b) p_x orbital. (c) p_y orbital. (d) p_z orbital. (e) d_{xy} orbital. (f) d_{yz} orbital. (g) d_{zx} orbital. (h) $d_{x^2-y^2}$ orbital. (i) $d_{3z^2-r^2}$ orbital.

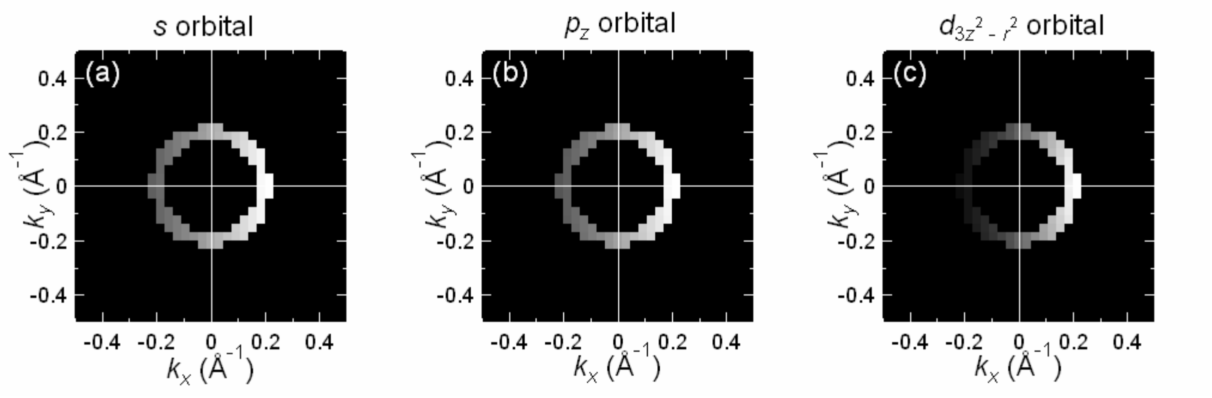

Fig. 6 Simulated PIADs of the FS weighted by the angular distribution from each atomic orbital. (a) *s* orbital. (b) p_z orbital. (c) $d_{3z^2-r^2}$ orbital.

well reproduced the experimental PIAD (Fig. 4). This result indicates that the Cu(111) Shockley surface state is composed of *s* orbital and/or *p*, *d* orbital normal to the surface. At present, the component ratio among these atomic orbitals is not clear. Further study such as incident angle dependence of the linearly polarized SR [3] is needed.

5. Summary

We have performed two-dimensional photoelectron spectroscopy measurements on Cu(111) surface. We have observed the Cu bulk Fermi surface and Cu 3*d* band, which have a three-fold symmetry due to the face-centered-cubic crystal structure of Cu. With the grazing incident geometry, we have successfully observed both the Cu bulk band and the Cu(111) Shockley surface state. The photoelectron intensity angular distribution from the Cu(111) Shockley surface state, however, was highly asymmetric due to the relation between the polarization vector of the incident synchrotron radiation and the atomic orbitals constituting the Cu(111) Shockley surface state. Compared with the simulated angular distributions from the atomic orbitals, this asymmetric distribution suggests that the Cu(111) Shockley surface state is composed of *s* orbital and/or *p*, *d* orbital normal to the surface.

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