Two-dimensional photoelectron spectroscopy study of Cu stepped surface

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Abstract

We have performed two-dimensional photoelectron spectroscopy measurement on Cu stepped surface. A two-dimensional photoelectron intensity angular distribution from the Cu stepped surface was obtained using a display-type analyzer and the linearly polarized synchrotron radiation (SR) with various polar angles of incidence. We have successfully observed both the bulk Fermi surface and the stepped surface state. A photoelectron intensity of the Cu stepped surface state increased with the incident angle of photon both for the step direction parallel and perpendicular to the linear polarization vector of SR light. Comparing with the simulated photoelectron intensities for *p* orbital normal to the stepped surface, a slight deviation was observed for the perpendicular geometry.

1. Introduction

Stepped surface of metals have regular arrays of atomic rows as step edges. These steps must have significant influences on the surface electronic states on the stepped surfaces. For example, one-dimensional electronic states have been found on the stepped surfaces; Ni(755) [1], Au(788) [2], and so on. Utilizing the stepped surface as substrate, nano-structures have also been fabricated, e.g., Co nanocluster on Cu(755) [3]. Especially, the Cu stepped surfaces vicinal to the (111) plane have been extensively studied because the Cu(111) surface has a free-electron-like two-dimensional electronic state [4]. The Cu stepped surface states have been classified into two types; the step modulation state and the terrace confined state [5, 6]. It has been shown that the propagating two-dimensional superlattice state (the steps act as superlattice) is realized when the terrace width is below ~ 20 Å, above which the stepped surface state is confined within the terrace, i.e., a quasi-one-dimensional quantum-well state [6]. In order to explain this transition, explanations such as the total energy and the interaction with bulk electronic states have been proposed but it remains unclear. On the other hand, the theoretical calculation has predicted that the p orbitals constituting the stepped surface states are tilted near the step edge and this tilt angle depends on the terrace width [7]. Therefore, the atomic orbital character is considered to have a relationship with the nature of the stepped surface states. Photoelectron spectroscopy (PES) measurements excited with linearly polarized photon are very useful to determine the symmetry of the atomic orbitals constituting the electronic state. 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) [8], one can analyze the component ratio among atomic orbitals [9]. 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 $4p$ orbitals with their axes pointing outward [10]. Furthermore, when the polar angle of the incident photon is varied, more precious information could be obtained [9]. In this work, we have performed 2D-PES measurements on Cu stepped surface taken at various polar angles of incidence using linearly polarized SR in order to determine the atomic orbital character constituting the Cu stepped surface state.

2. Experiment

The experiment was performed at the linearly polarized soft x-ray beamline BL-7 of
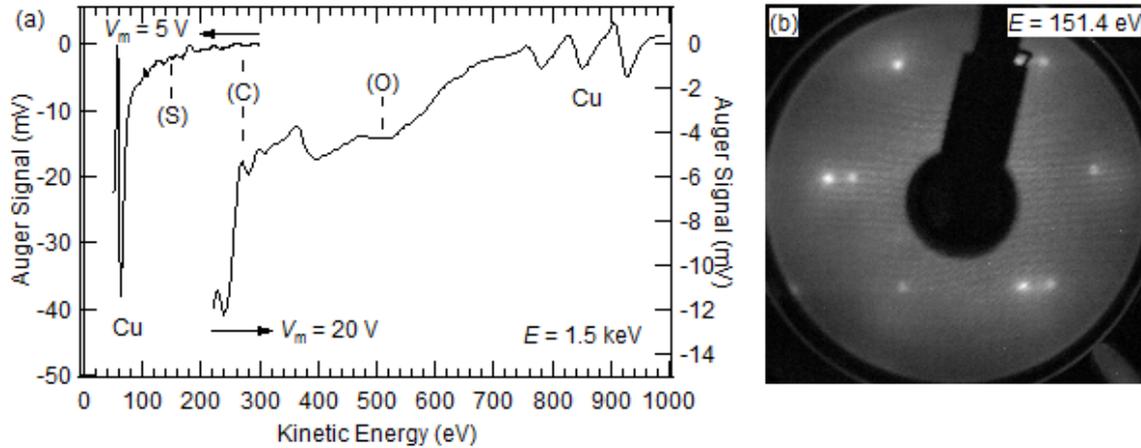
Fig. 1 AES spectrum (a) and LEED pattern (b) of the Cu stepped surface.

SR center, Ritsumeikan University [11]. The electric vector of the linearly polarized SR light was in the horizontal plane. The sample was cut from a (111)-oriented Cu single-crystal rod and polished mechanically and electrochemically. The Cu stepped surface was cleaned *in situ* by repeated cycles of Ar^+ bombardment and annealing to ~ 500 °C in an ultrahigh-vacuum chamber. The surface quality was checked by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) measurements as shown in Fig. 1. The AES spectrum hardly shows the S, C, nor O signals. The LEED pattern shows sharp 1×1 spots, some of which are split due to the step periodicity. By analyzing the split width, the step periodicity (or terrace width) was estimated to be d ~ 13 Å and the tilt angle of ~10°. The 2D-PES measurements were performed at room temperature under ultrahigh vacuum of ~1×10^{-8} Pa using a DIANA [8, 12] with SR light. 2D-PIAD and a stereo profile of the Fermi surface (FS) are efficiently obtained by using DIANA. 2D-PIAD of this experiment was collected
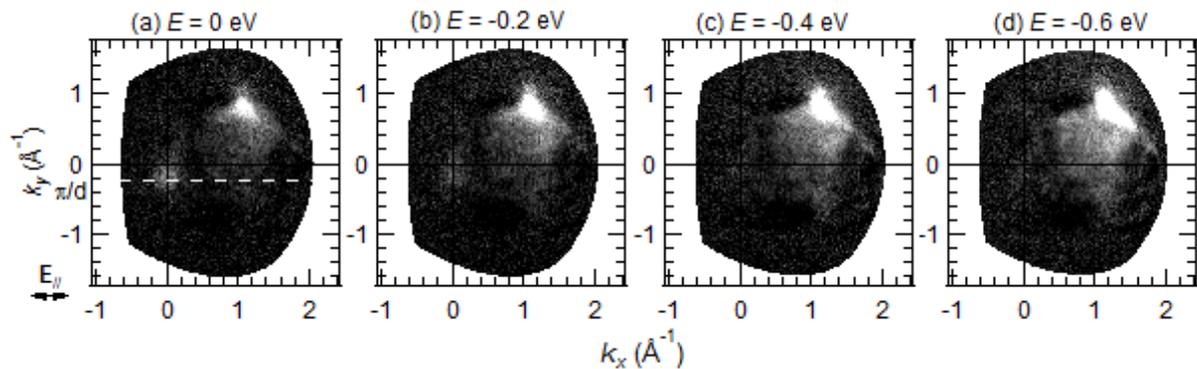
Fig. 2 2D-PES result of the Cu stepped surface taken with $h\nu$ = 21 eV. The PIADs at E = 0.0 eV (a), -0.2 eV (b), -0.4 eV (c), and -0.6 eV (d). The electric vector of the incident light is in the horizontal direction.

by energy window of 100 meV. Typical acquisition time for one PIAD was 30 sec. The total energy resolution was about 300 meV. The angular resolution was about 1°.

3. Results

Figure 2 shows the series of PIAD from the Cu stepped surface taken with $h\nu$ = 21 eV. The photoelectron intensity is displayed on a gray scale. The linearly polarized SR ($E_{//}$ // k_x) is incident from $+k_x$ direction with the angle of 40° from k_z axis (step surface normal). As in the case of previous angle-resolved photoelectron spectroscopy (ARPES) results of Cu(111) surface (the terrace plane of this Cu stepped surface) taken with He I source ($h\nu$ = 21.2 eV) [4], the FS of the Cu bulk band around (k_x, k_y) ~ (1, 1) [Å^{-1}] was successfully observed at E = 0 eV. The PIADs change with decreasing the energy, reflecting the Cu bulk band dispersion. Around (k_x, k_y) ~ (0, -0.24[= $-\pi/d$]) Å^{-1} (the surface M point), the Cu stepped surface state was also successfully observed. The stepped surface state appeared at the surface M point, which is consistent with the previous work on the Cu stepped surface [13]. With decreasing the energy, the Cu stepped surface state disappears below ~ -0.4 eV. This observation is also consistent with the fact that the Cu(111) Shockley surface state has a parabolic band dispersion with the band bottom energy of ~ -0.4 eV [4], since the terrace of this Cu step surface
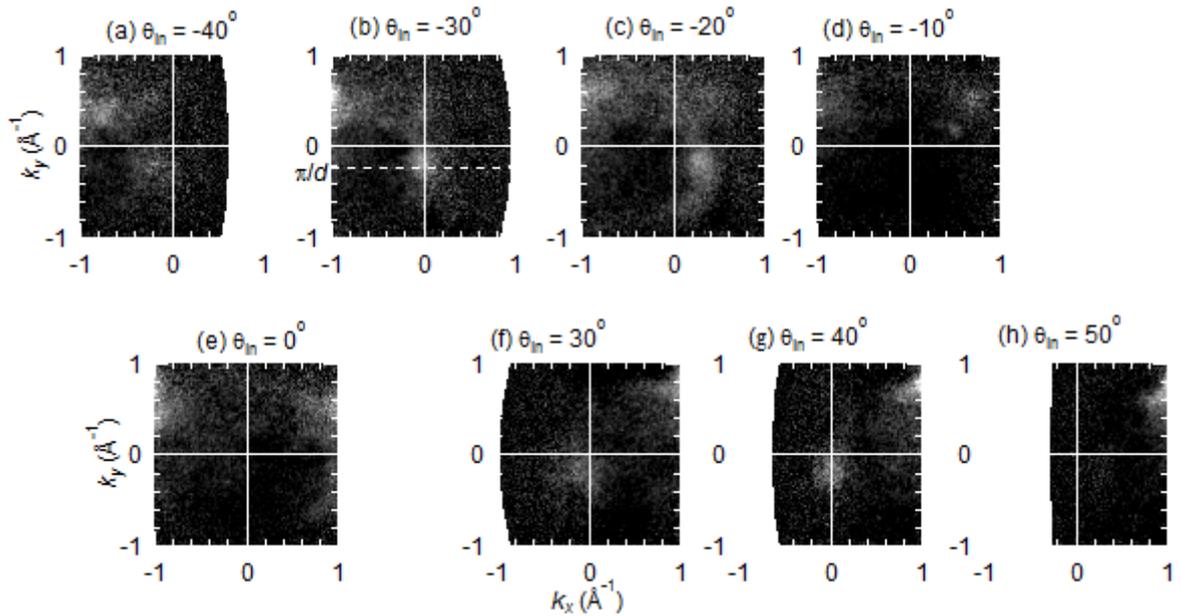
Fig. 3 PIADs of FS from the Cu stepped surface state taken at various polar angles of incidence. (a) θ_{in} = -40°. (b) θ_{in} = -30°. (c) θ_{in} = -20°. (d) θ_{in} = -10°. (e) θ_{in} = 0°. (f) θ_{in} = 30°. (g) θ_{in} = 40°. (h) θ_{in} = 50°. The step direction and the surface parallel component of the electric vector of the incident photon are in the horizontal direction.

is composed of the (111) plane. It should be noted that the energy of the band bottom increases on the stepped surface [3, 13] compared with that on the Cu(111) surface, which may make the circular shape of FS smeared to be closed circle as shown in Fig. 2.

In order to see the atomic orbital character, we have performed the incident angle dependent 2D-PES measurements. The surface parallel component of the electric vector was set to either parallel (Fig. 3) or perpendicular (Fig. 4) to the step direction. In both the parallel and perpendicular geometries, the stepped surface state appears with increasing the incident angle, $|\theta_{in}|$.
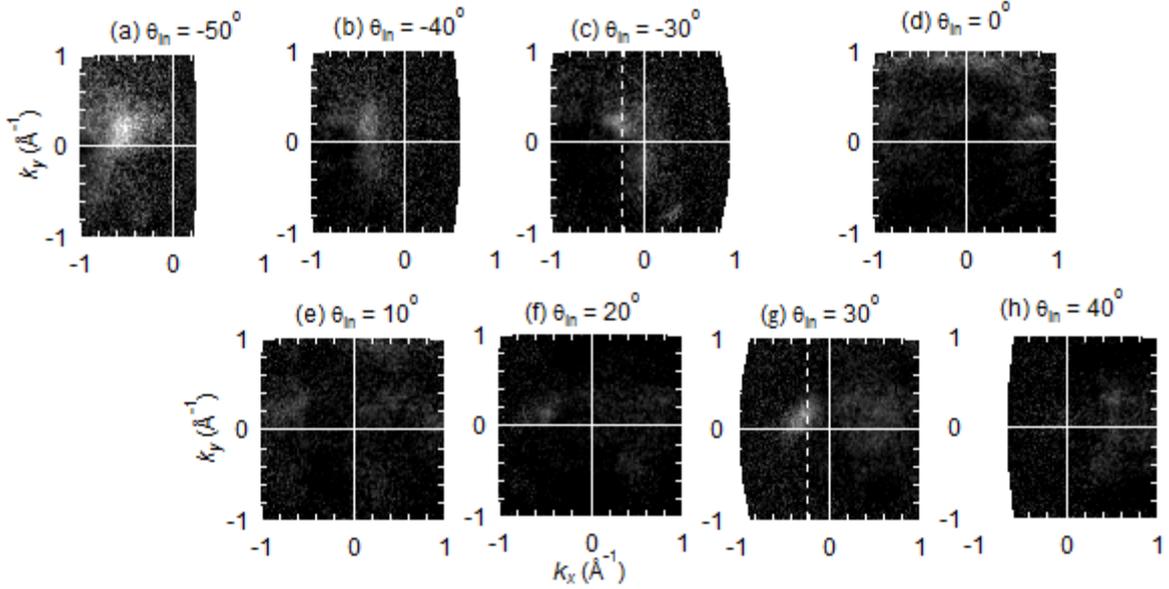
Fig. 4 PIADs of FS from the Cu stepped surface state taken at various polar angles of incidence. (a) θ_{in} = -50°. (b) θ_{in} = -40°. (c) θ_{in} = -30°. (d) θ_{in} = 0°. (e) θ_{in} = 10°. (f) θ_{in} = 20°. (g) θ_{in} = 30°. (h) θ_{in} = 40°. The step direction is the vertical direction, while the surface parallel component of the electric vector of the incident photon is in the horizontal direction.

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 $I(\theta_k, \phi_k)$ in the direction of polar angle θ_k and azimuth angle ϕ_k can be expressed as[10, 14]:

$$I(\theta_k, \phi_k) \sim D^1(k_{//}) \ |\Sigma_v \ A_v|^2,$$

where $D^1(k_{//})$ is the one-dimensional density of states [15] and A_v is the "angular distribution from the v–th atomic orbital" [16]. Assuming that the Cu stepped surface state has a circular FS with the radius of 0.2 Å^{-1} at the surface M point [13] and the
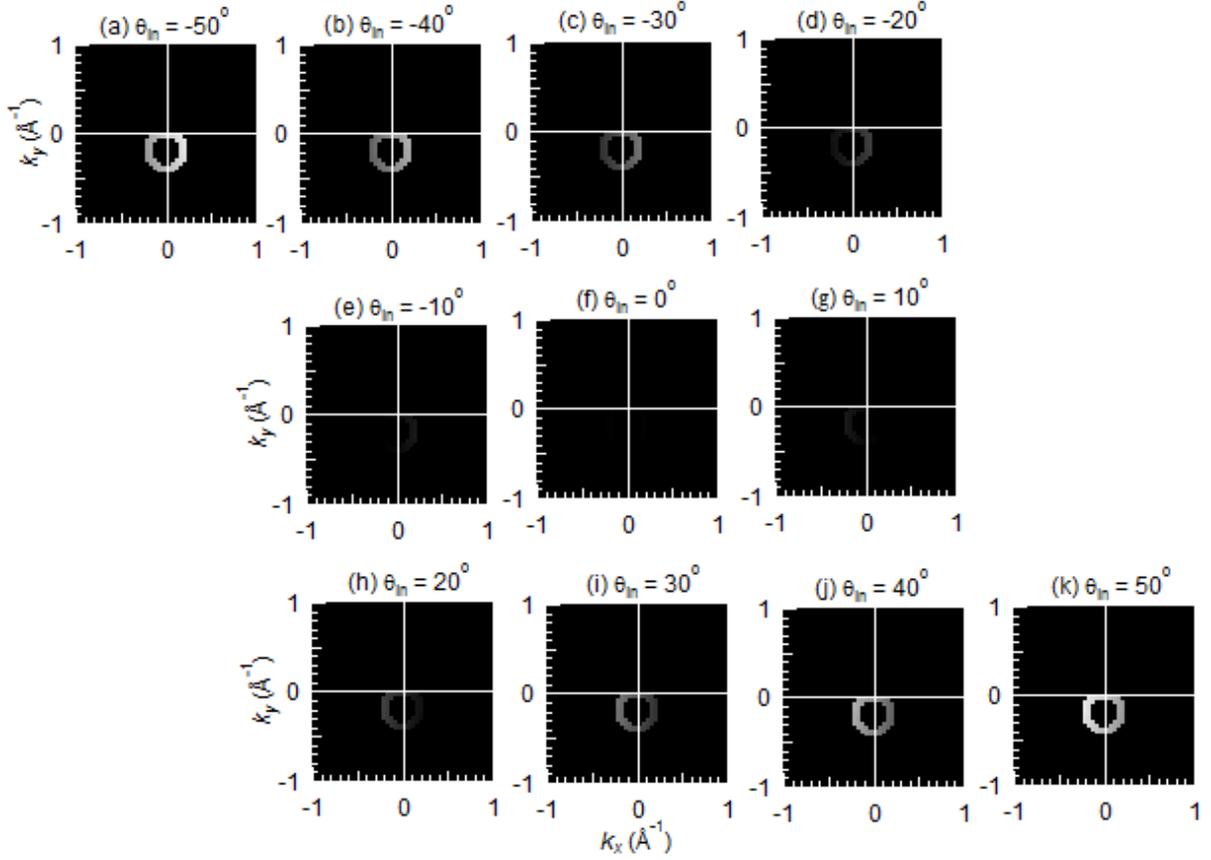
Fig. 5 Simulated PIADs of FS from the Cu stepped surface state taken at various polar angles of incidence. (a) θ_{in} = -50°. (b) θ_{in} = -40°. (c) θ_{in} = -30°. (d) θ_{in} = -20°. (e) θ_{in} = -10°. (f) θ_{in} = 0°. (g) θ_{in} = 10°. (h) θ_{in} = 20°. (h) θ_{in} = 30°. (h) θ_{in} = 40°. (h) θ_{in} = 50°. The step direction and the surface parallel component of the electric vector of the incident photon are in the horizontal direction.

work function is 4.7 eV [10], the PIADs taken with $h\nu$ = 21 eV for p_z atomic orbitals were simulated. Here, we set the step surface normal to z axis and set the surface parallel component of the electric vector of the incident photon to x axis, and the step direction was set to either parallel (Fig. 5) or perpendicular (Fig. 6) to it. The simulated PIADs qualitatively reproduced the experimental PIADs taken at various polar angles of incidence (Figs. 3 and 4), that is, the photoelectron intensity of the Cu stepped surface state increased with the incident angle, $|\theta_{in}|$ in both parallel and perpendicular geometries. In order to compare the experimental data with simulated data more quantitatively, the total photoelectron intensity of the Cu stepped surface state was estimated and rescaled (Fig. 7). For the parallel geometry, the incident angle dependence of the experimental intensity is well reproduced by the simulation for p_z atomic orbital as shown in Fig. 7(a). For the perpendicular geometry, however, there seems to be a slight deviation around $\theta_{in} \sim 20°$. This behavior would be explained if the
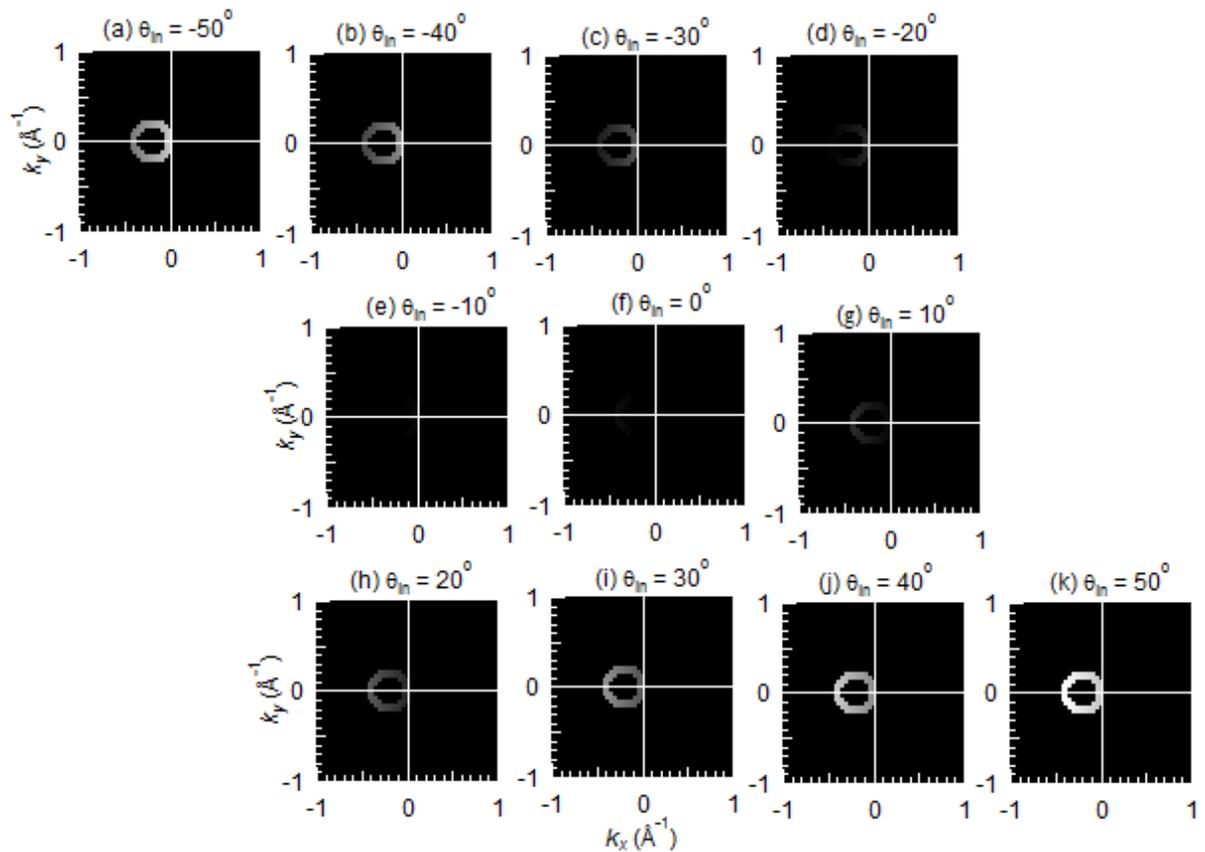
Fig. 6 Simulated PIADs of FS from the Cu stepped surface state taken at various polar angles of incidence. (a) θ_{in} = -50°. (b) θ_{in} = -40°. (c) θ_{in} = -30°. (d) θ_{in} = -20°. (e) θ_{in} = -10°. (f) θ_{in} = 0°. (g) θ_{in} = 10°. (h) θ_{in} = 20°. (h) θ_{in} = 30°. (h) θ_{in} = 40°. (h) θ_{in} = 50°. The step direction is the vertical direction, while the surface parallel component of the electric vector of the incident photon is in the horizontal direction.
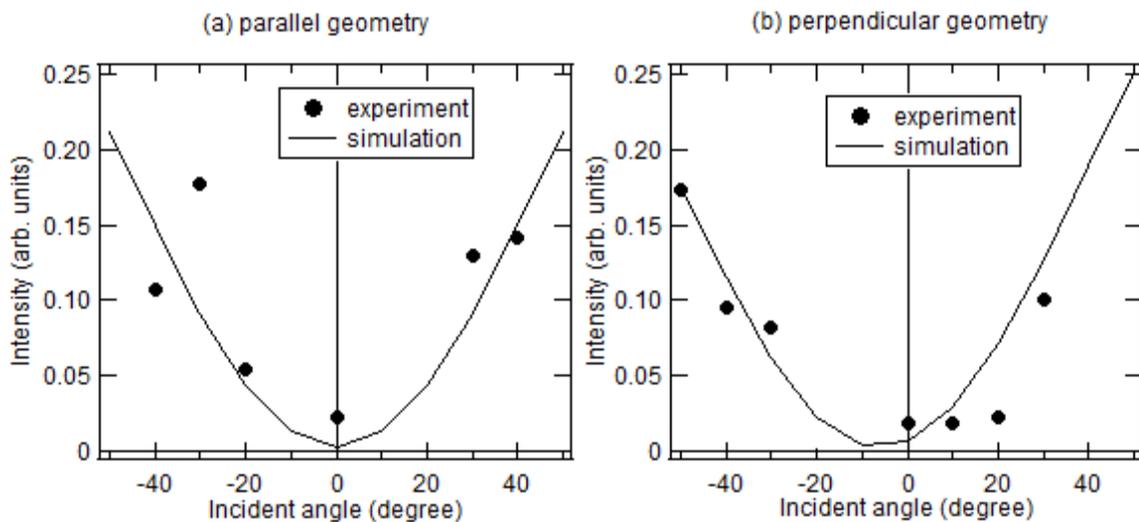
Fig. 7 Photoelectron intensity of the Cu stepped surface state excited at various incident angles. The step direction is parallel (a) or perpendicular (b) to the surface parallel component of the electric vector of the incident photon.

p_x orbital contributed to the stepped surface state, that is, the p orbital tilted perpendicular to the step direction. Further study is needed to elucidate the atomic orbital character more precisely.

5. Conclusions

We have performed two-dimensional photoelectron spectroscopy measurements on Cu stepped surface. Incident angle dependent photoelectron intensity of the Cu stepped surface state showed a similar behavior even when the step direction was set to parallel or perpendicular to the linear polarization vector of SR light. Comparing with the simulation for p orbital normal to the stepped surface, a slight deviation was observed for the perpendicular geometry.

References

[1] H. Namba, K. Yamamoto, T. Ohta, and H. Kuroda, J. Electron Spectrosc. Relat. Phenom. **88-91**, 707 (1998).

[2] J. E. Ortega, A. Mugarza, V. Repain, S. Rousset, V. Pérez-Dieste, and A. Mascaraque, Phys. Rev. B **65**, 165413 (2002).

[3] Koji Ogawa, Koji Nakanishi, and Hidetoshi Namba, Surf. Sci. **566-568**, 406 (2004).

[4] F. Reinert and S. Hüfner, New J. Phys. **7**, 97 (2005).

[5] J. E. Ortega, S. Speller, A. R. Bachmann, A. Mascaraque, E. G. Michel, A. Närmann, A. Mugarza, A. Rubio, and F. J. Himpsel, Phys. Rev. Lett. **84**, 6110 (2000).

[6] F. Baumberger, M. Hengsberger, M. Muntwiler, M. Shi, J. Krempasky, L. Patthey, J. Osterwalder, and T. Greber, Phys. Rev. Lett. **92**, 196805 (2004).

[7] R. Eder and H. Winter, Phys. Rev. B **70**, 085413 (2004).

[8] H. Daimon, Rev. Sci. Instrum. **59**, 545 (1988).

[9] H. Daimon, M. Kotsugi, K. Nakatsuji, T. Okuda, and K. Hattori, Surf. Sci. **438**, 214 (1999).

[10] F. Matsui, H. Miyata, O. Rader, Y. Hamada, Y. Nakamura, K. Nakanishi, K.

Ogawa, H. Namba, and H. Daimon, Phys. Rev. B **72**, 195417 (2005).

[11] Y. Hamada, F. Matsui, Y. Nozawa, K. Nakanishi, M. Nanpei, K. Ogawa, S. Shigenai, N. Takahashi, H. Daimon, and H. Namba, AIP Conf. Proc. **879**, 547 (2007).

[12] N. Takahashi, F. Matsui, H. Matsuda, Y. Hamada, K. Nakanishi, H. Namba, and H. Daimon, J. Electron Spectrosc. Relat. Phenom. **163**, 45 (2008).

[13] F. Baumberger, T. Greber, and J. Osterwalder, Phys. Rev. B **64**, 195411 (2001).

[14] H. Daimon, S. Imada, H. Nishimoto, and S. Suga, J. Electron Spectrosc. Relat. Phenom. **76**, 487 (1995).

[15] T. Grandke, L. Ley, and M. Cardona, Phys. Rev. B **18**, 3847 (1978).

[16] S. Goldberg, C. Fadley, and S. Kono, J. Electron Spectrosc. Relat. Phenom. **21**, 285 (1981).