Atomic-orbital analysis of the Cu(111) surface state by two-dimensional photoelectron spectroscopy with linearly polarized synchrotron radiation: Polar angle dependence of incident photon

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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 various polar angles of incidence. With the grazing incident geometry, we have successfully obtained the PIAD from the Cu(111) Shockley surface state. However, its PIAD was highly asymmetric and dependent on the polar angle of incidence. Compared with the simulated PIADs, incident angle dependence of PIADs suggests that the Cu(111) Shockley surface state is composed of *s* orbital and/or *p* orbital normal to the surface.

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 $\varepsilon_0 \sim -0.4$ eV, the effective band mass of $m^*/m_e \sim 0.4$, and the Fermi wave number of $k_\mathrm{F} \sim 0.2$ 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].

Although ARPES is an indispensable tool for elucidating the electronic structure, ARPES spectra sometimes shows symmetry-broken patterns due to the matrix element. Recently, a complex behavior of the photoelectron intensity distribution of the Cu(111) Shockley surface state was observed with light polarization and energy [2]. They explained that this is due to the matrix element effect connected to the *p*-*d* transition channel from the *p*-orbital of the surface state to the *d*-orbital of the final state.

Thus, 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) [3], one can analyze the component ratio among atomic orbitals [4]. 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 [5].

Furthermore, when the polar angle of the incident photon is varied, more precious information could be obtained [4]. In this work, we have performed 2D-PES measurements on Cu(111) surface taken at various polar angles of incidence using 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 [6]. 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 $^\circ$C. 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 ~1×10^{-8} Pa using DIANA [3, 7]. 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 90 sec. The photon energy was 22.5 eV. The total energy resolution was about 300 meV. The angular resolution was about 1°.

3. Results

Figure 1 summarizes the series of PIAD at various energies taken at various polar angles of incidence. The linearly polarized SR ($\boldsymbol{E}_{//}$ // k_x) is incident from $-k_x$ direction with the angle of 10° - 50° from k_z axis. As in the case of previous ARPES results taken with He I source ($h\nu$ = 21.2 eV) [1], the FS of the Cu bulk band around k_x ~ -1.5 Å^{-1} was successfully observed for every PIAD at E = 0 eV. The PIADs change with decreasing the energy, reflecting the Cu bulk band dispersion. On the other hand, the Cu(111) Shockley surface state appears only when the incident angle increases more than ~20°. This is consistent with the fact that the Cu(111) Shockley surface state has the symmetry forbidden for *s*-polarized geometry due to the matrix element effect by the polarization of the excited light [2]. With decreasing the energy, the Cu(111) Shockley surface state shrinks to the center ($k_x = k_y = 0$ Å^{-1}) and 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 [1]. Thus, with the grazing incident geometry, we have successfully observed the Cu(111) Shockley surface state.

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 for more than ~20° seem to have the same circular FS (dashed circle in Fig. 2). For the incident angles of 20° and 30°, however, its photoelectron intensity is highly asymmetric, i.e., the photoelectron intensity in the right hand side region of the circular FS is strong [1, 2]. By rotating the sample around the (111) surface normal, we have found that the photoelectron intensity in the right hand side region of the circular FS was always strong (not shown). 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, indicating that the Cu(111) Shockley surface state is composed of *s* orbital and/or *p, d* orbital normal to the surface. For the incident angle of 40° and 50°, although the shape is not clear, the circular FS seems to be observed, i.e., the intensity asymmetry seems to disappear.

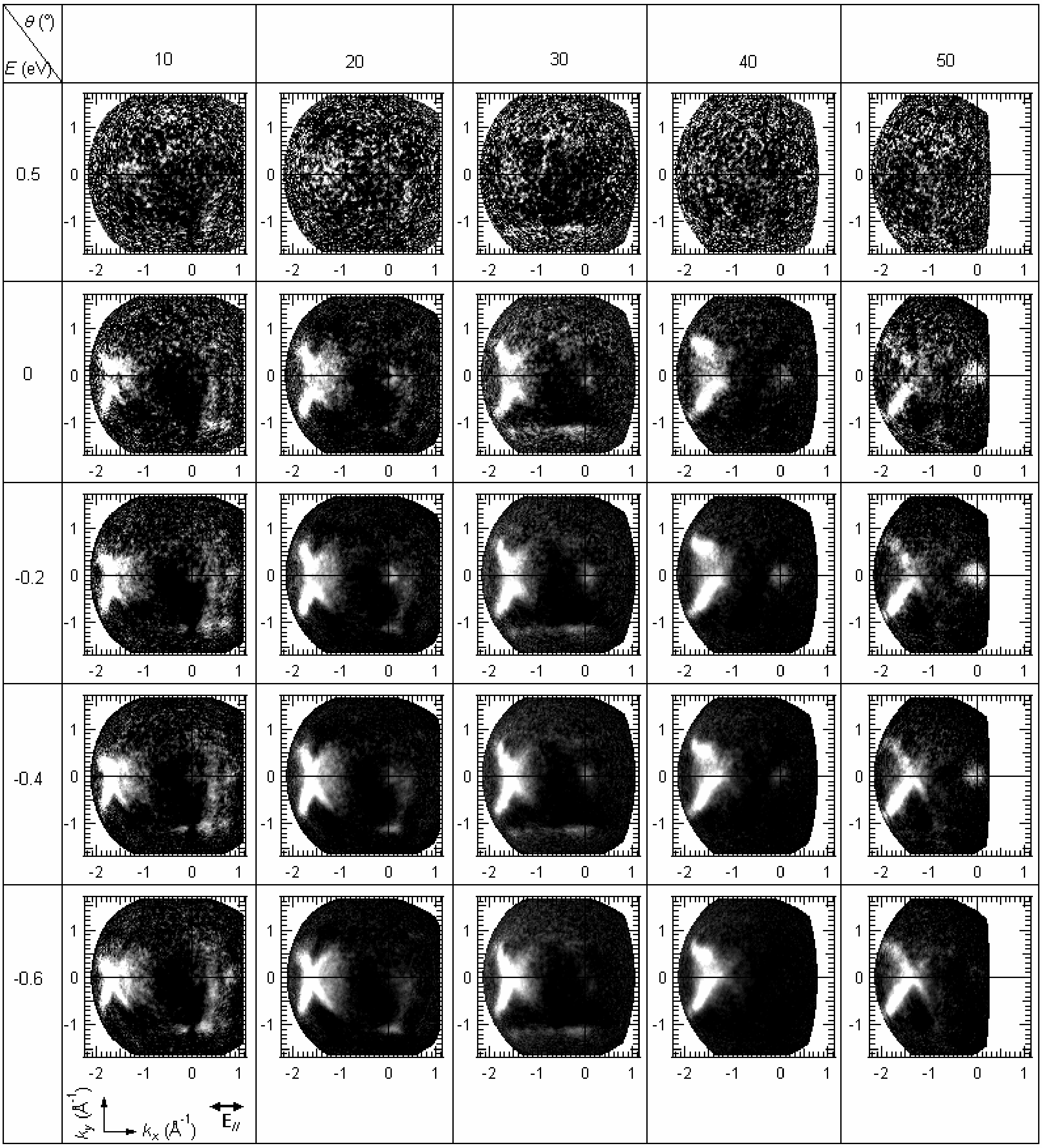

Fig. 1 PIADs from Cu(111) at various energies taken at various polar angles of incidence. The energies were varied with 0.5 eV, 0 eV, -0.2 eV, -0.4 eV, and -0.6 eV. The polar angles of incidence were varied with 10°, 20°, 30°, 40°, and 50°. The surface parallel component of the electric vector of the incident photon is in the horizontal direction.

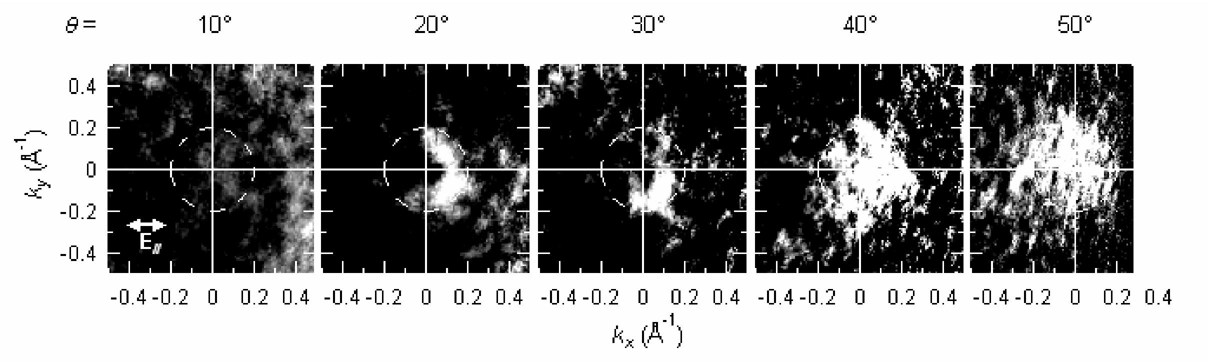

Fig. 2 PIADs of FS from the Cu(111) Shockley surface state taken at various polar angles of incidence. The polar angles of incidence were varied with 10°, 20°, 30°, 40°, and 50°. The dashed circle with the radius of ~ 0.2 Å^{-1} is also shown. The surface parallel component of the electric vector of the incident 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[4, 8]:

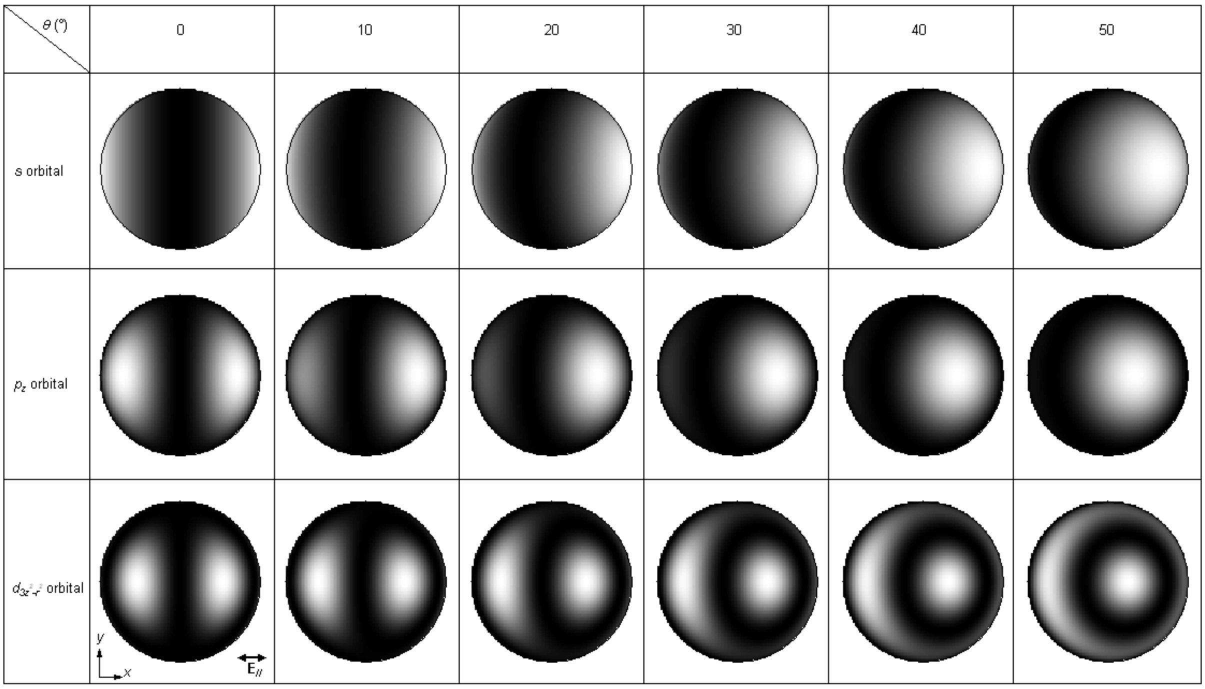

Fig. 3 Calculated angular distributions from s, p_z, and $d_{3z^2-r^2}$ atomic orbitals excited at various incident angles. The linearly polarized light is incident from -x direction with the angle of 0°, 10°, 20°, 30°, 40°, and 50° from z axis. The surface parallel component of the electric vector of the incident photon is in the horizontal direction.

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

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 s, p_z, and $d_{3z^2-r^2}$ atomic orbitals excited at various incident angles are shown in Fig. 3. As in the experimental condition, the linearly polarized SR ($\boldsymbol{E}_{//}$ // x) is incident from -x direction with the angle of 0° - 50° from z axis. Here, we set the [111] direction to z axis. As shown in Fig. 3, 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. At a certain incident angle, these angular distributions from s, p_z, and $d_{3z^2-r^2}$ atomic orbitals do no change with the rotation around z axis (not shown). In this case, it is very difficult to distinguish the s, p_z, and $d_{3z^2-r^2}$ atomic orbitals. On the other hand, the incident polar angle dependences of the s, p_z, and $d_{3z^2-r^2}$ atomic orbitals seem to be different as shown in Fig. 3. Therefore, comparing the experimental PIAD with these angular distributions from the atomic orbitals, one can determine the atomic orbitals constituting the electronic state [4].

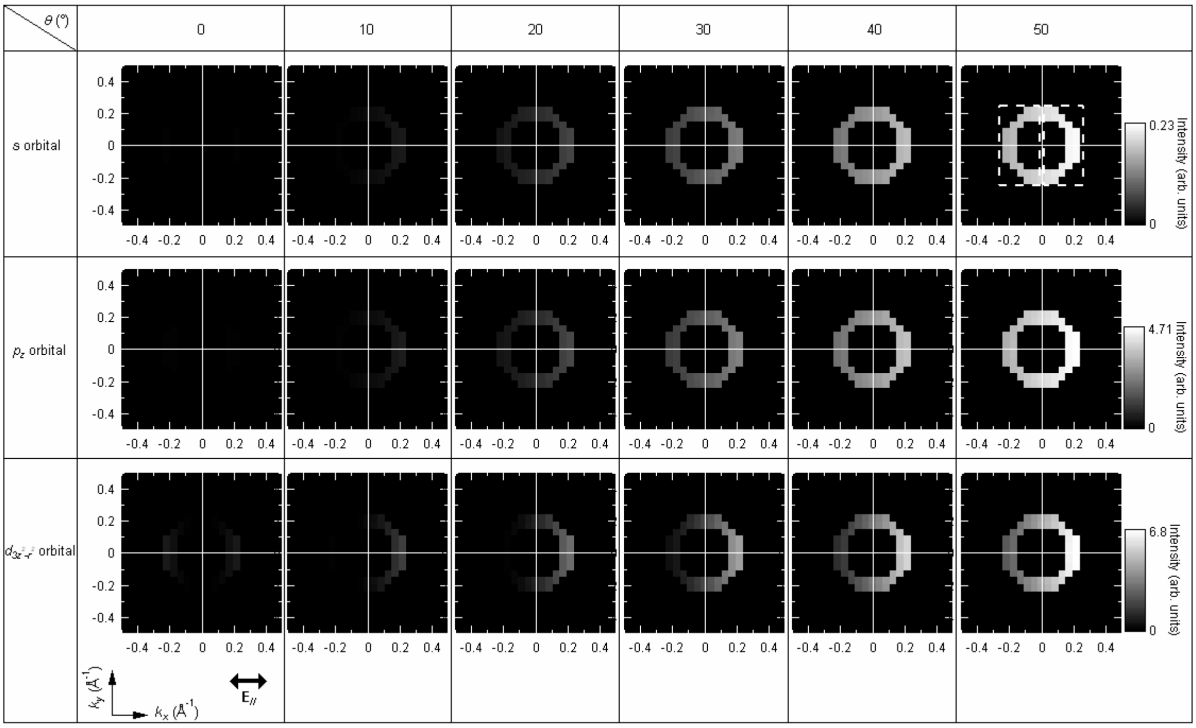

Fig. 4 Simulated PIADs of FS from the Cu(111) Shockley surface state taken at various polar angles of incidence. The Cu(111) Shockley surface state is assumed to be composed of either s, p_z, or $d_{3z^2-r^2}$ atomic orbitals. The polar angles of incidence were varied with 0°, 10°, 20°, 30°, 40°, and 50°. The surface parallel component of the electric vector of the incident photon is in the horizontal direction.

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 [5], the PIADs taken with $h\nu$ = 22.5 eV for s, p_z, and $d_{3z^2-r^2}$ atomic orbitals are simulated as shown in Fig. 4. The simulated PIADs well reproduced the experimental PIADs taken at various polar angles of incidence (Fig. 2). For incident angle of 10°, the intensity is very weak. By increasing the incident angle to ~20°-30°, the intensity of right hand side region becomes strong. For the incident angle of ~40°-50°, the intensity of left hand side region also appears and the circular shape is seen. In order to compare the experimental data with simulated data more quantitatively, the intensity ratios of right to left regions, as indicated in Fig. 4, were estimated (Fig. 5). Incident angle dependences of experimental intensity ratio are well reproduced by the simulations for s and p_z atomic orbitals as shown in Fig. 5.

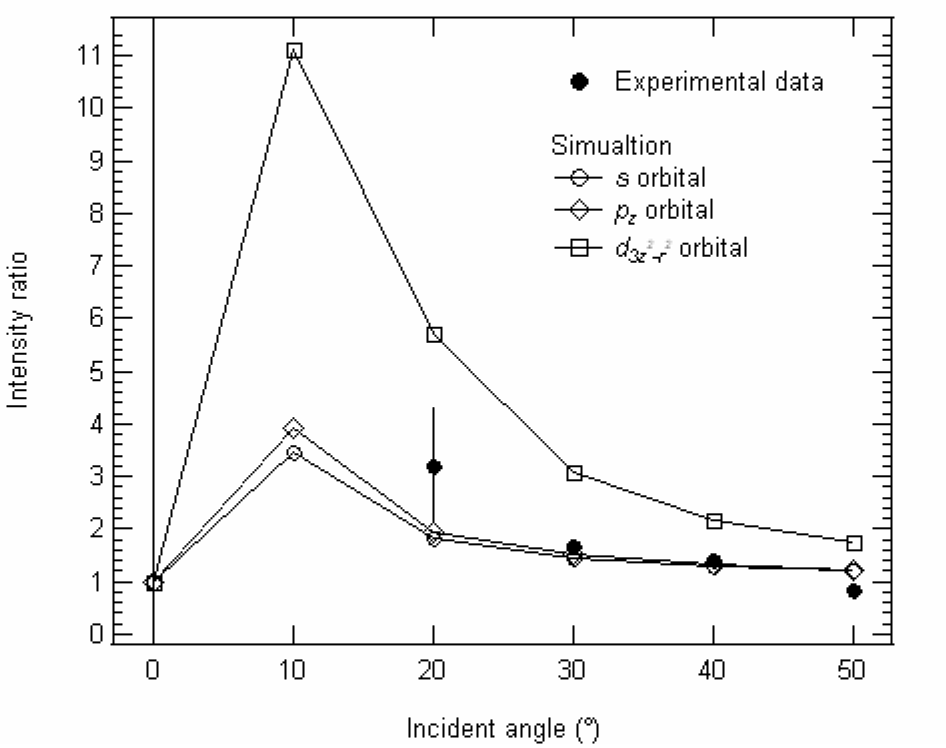

Fig. 5 Intensity ratio of right to left regions for the Cu(111) Shockley surface state excited at various incident angles.

5. Conclusions

We have performed two-dimensional photoelectron spectroscopy measurements on Cu(111) surface taken at various polar angles of incidence. 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 and dependent on the polar angles of incidence 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 and its polar angle dependence of incident photon suggest that the Cu(111) Shockley surface state is composed of *s* orbital and/or *p* orbital normal to the surface.

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References

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

[2] M. Mulazzi, G. Rossi, J. Braun, J. Minár, H. Ebert, G. Panaccione, I. Vobornik, and J. Fujii, Phys. Rev. B **79**, 165421 (2009).

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

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

[5] 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).

[6] 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).

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

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

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

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