Electronic Structure of Stepped Cu(911) Surface Studied by Angle-Resolved Ultraviolet Photoelectron Spectroscopy at SORIS Beamline

Koji Ogawa, Koji Tsuchida, Koji Nakanishi and Hidetoshi Namba

Abstract

We have investigated the electronic structure of stepped Cu(911) in the expectation of creating a new surface material with new one-dimensional surface states by angle-resolved ultraviolet photoelectron spectroscopy using synchrotron radiation(SR-ARUPS). Since Cu(911) has (111) planes as steps, we expected that (111)-derived *sp* surface state is induced just as on planar Cu(111) and that the surface state has one-dimensional nature being localized at steps. In SR-ARUPS spectra, however, we observed only a single peak whose dispersion revealed to be the bulk *sp*-band peak and so there induced no new surface state on Cu(911). The reason for this is discussed and is concluded to be most probably an energy shift of the surface state above the Fermi level.

Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan.

Introduction

The properties and nature of surface states on metals, which are localized in the very vicinity of the surfaces, strongly depend on the atomic structure of the surfaces where they are induced. On planar surfaces such as the closest packed surfaces of planar Cu(111) and Au(111), the *sp* surface states have a high in-plane isotropy being two-dimensional. The two-dimensional nature of such surface states is evident from identical energy dispersions in two orthogonal directions and circular Fermi surfaces obtained by means of angle-resolved ultraviolet photoelectron spectroscopy(ARUPS)[1]. When the isotropy in the surface structure is hindered by, for example, a regular array of surface steps, the anisotropy must have some influence on the surface states. On stepped Ni(755) which has a regular array of steps, ARUPS spectra revealed that the two-dimensional surface state retains the nature, but a new anisotropic state is induced[2,3]. Since the new state disperses only along the steps, the state has one-dimensional nature. Moreover, alkali metals adsorbed at the steps more sensitively reduced the intensity of the one-dimensional-state peak than that of the two-dimensional one in the UPS spectra. So the new state was concluded to localize at the steps. On stepped Cu(755) which has the same atomic structure as Ni(755), on the other hand, no new step state is not found, while we observed only the two-dimensional *sp* surface state[4].

The results on Cu(755) posed important questions about the two-dimensional surface state. One is why the surface state on Cu(755) still has a two-dimensional nature despite of the highly anisotropic surface structure. We attributed the *sp* nature of the surface state to the reason for delocalization[4]. It is worth of consideration, furthermore, if the surface state retains the two-dimensional nature even on more anisotropic surfaces. Baumberger *et al.* reported that the surface state is still two-dimensional on Cu(221) whose terrace width is only four-atomic-row wide[5]. We, then, determined to investigate the surface state on one of the most anisotropic surface which has (111) planes of only two-atomic-row wide as steps. One of such stepped surface is Cu(911) and on this stepped surface we expect the surface state become one-dimensional. We report in the following sections of the present paper the results of ARUPS measurement on Cu(911) using synchrotron radiation for excitation.

Experimental

Cu(911)[=5(100)×(111)] is inclined by 8.9° with respect to (100) towards [111] (Fig. 1).   The calculated average terrace width is 11.6 Å.   The step direction is along the [0 $\bar{1}$1] direction.   The samples were cut from a (111)-oriented single-crystal rod and polished mechanically and electrochemically.   We cleaned the samples by repeated cycles of Ar$^+$ ion sputtering at $\leq$1 keV and annealing at 780 K in a sample-preparation chamber whose base pressure is below 1×10^{-10} Torr.   We confirmed the surface cleanliness and crystallinity by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) patterns (Fig. 2).
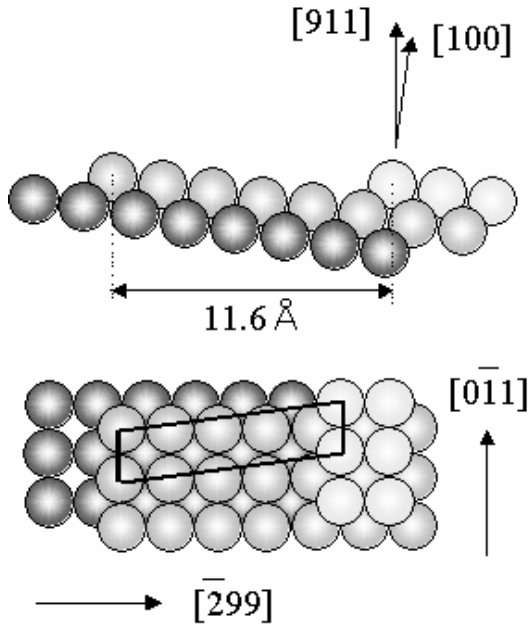

Fig. 1. Hard-Sphere model of ideal surface atomic configurations for stepped Cu(911). Primitive surface unit cells are indicated by a parallelogram.
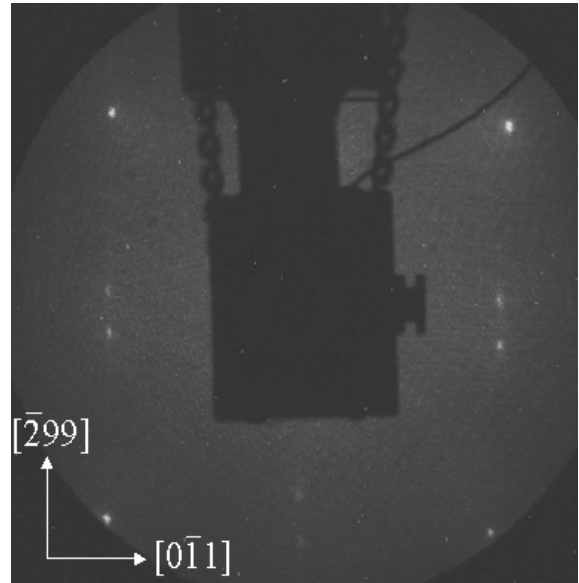
Fig. 2. LEED pattern from stepped Cu(911) at $E_k=-123$ eV.

Measurements of SR-ARUPS were carried out at the SORIS Beamline, a compact VUV beamline for high-resolution photoelectron spectroscopy at the SR Center, Ritsumeikan University[6].   The available photon energy is from 5 to 700 eV. SR-ARUPS spectra were measured at room temperature using a high-resolution electron energy analyzer[7].   The total energy resolution of the monochromator and the energy analyzer was estimated to be about 30 meV for the present measurements. The acceptance angle of the analyzer for photoelectrons was set to be ±2°.   The angle between the incident photon and the axis of the energy analyzer was fixed to be 55°. The incident photon is *p*-polarized in oblique incidence.   In the present study, the samples were rotated for the measurements of angular distribution of photoelectrons. The incident angle of photons linearly polarized in the horizontal plane is |55°-θ_e| and

varied with θ_e, where θ_e is the emission angle measured from [100]. The azimuth angle is changed also by rotating samples around the terrace normal of [100] in vacuum. When the steps are parallel and perpendicular to the plane of incidence, the setup is referred as the parallel and perpendicular configurations, respectively.

Results and Discussion

Figure 3 is the angular dependence of the photoemission spectra on stepped Cu(911) taken around the $\bar{M}$ point of the surface Brillouin zone at hv=11 eV in (a) the parallel and (b) the perpendicular configurations. The abscissa is the binding energy and the ordinate the intensity normalized by the storage-ring current. The emission angles of photoelectron are indicated in the figure. The binding-energy region just below the Fermi level alone is shown where the surface state on planar Cu(111) is observed. Accordingly, in Fig. 3(a) we observed a single peak dispersing downward from the Fermi level with the increase of emission angle in the parallel configuration. The dispersion of this peak, which is closely investigated at different photon energies, agrees with that of the bulk sp-band peak on planar Cu(100) as shown in Fig. 4[8]. Thus, we assigned the observed peak to be from the bulk sp band. The dispersion of other peaks is also in good agreement.

In the perpendicular configuration, however, the peak broadens almost twice

Fig. 3. ARUPS spectra on clean stepped Cu(911) taken at hv=11 eV in (a) the parallel and (b) perpendicular configurations.

as much as in the parallel configuration. This peak broadening suggests the existence of other overlapping peaks. If of surface origin as we expected, the possible overlapping peaks may be more sensitive than the bulk sp-band peak. We, then, attempt to distinguish the former from the latter by making use of the different
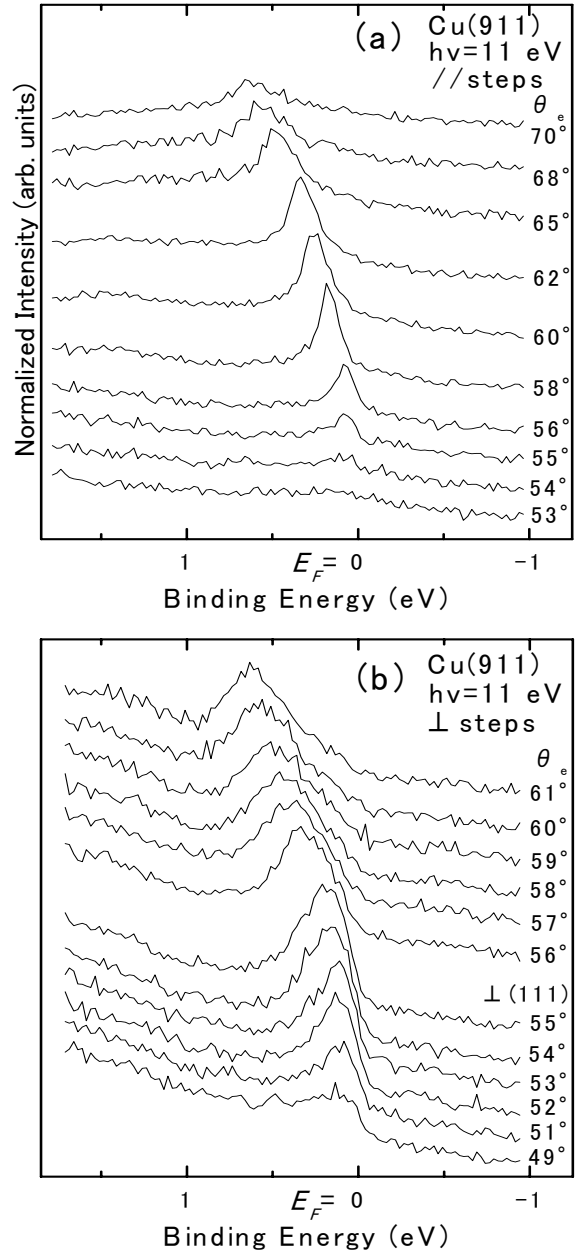
sensitivity to adsorbates such as oxygen. Figure 5 shows the spectra at different oxygen adsorption at various exposures in both the parallel and perpendicular configurations. Upon oxygen exposure, the peak in the parallel configuration decreased monotonously as in Fig. 5(a). Against our expectation, Fig. 5(b) shows that the peak in the perpendicular configuration also decreased monotonously with no sign of overlapping peaks. This is also demonstrated by the difference spectra shown in Fig. 6. So we conclude that we observed only one single bulk sp-band peak.
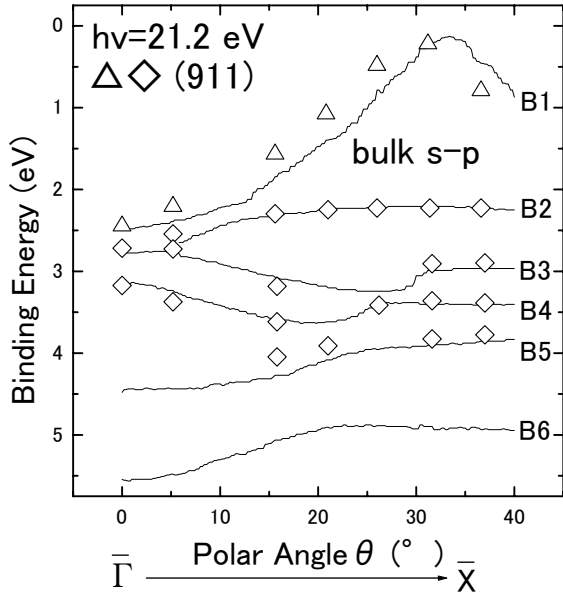

Fig. 4. Dispersion relation of the electronic states in the parallel configuration on clean stepped Cu(911) (symbols) and on planar Cu(100) (solid lines). The triangles correspond to the bulk sp-band peak in Fig. 3(a).
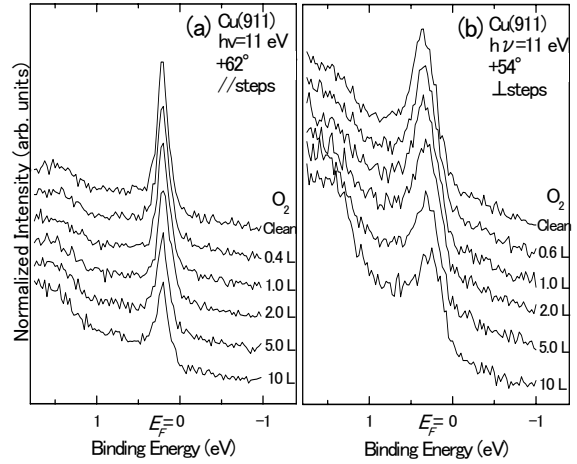

Fig. 5. ARUPS spectra taken at hv=11 eV in (a) the parallel and (b) perpendicular configurations at various exposures of oxygen from 0.4 to 10-L on stepped Cu(911).
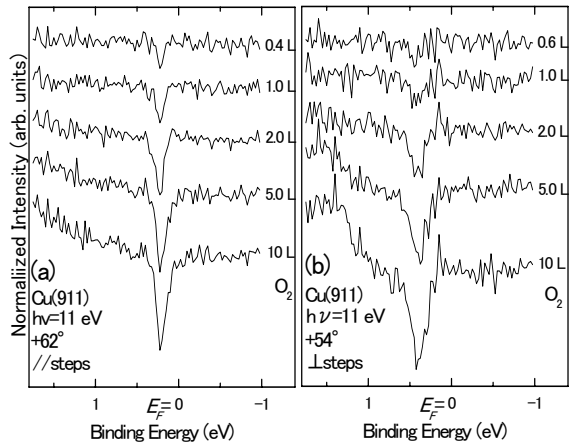

Fig. 6. Difference spectra [emission of the contaminated surface subtracted from that of the clean surface] for the stepped Cu(911) taken at hv=11 eV.

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In the preceding arguments, we found no one-dimensional state of surface origin localized at the steps in the UPS spectra of stepped Cu(911). This fact can have three different implications. One is simply that the surface electrons do not see the steps as a surface so that no surface state is induced on Cu(911). The other is that because of its delocalized nature the *sp* surface state on the planar (111) can not be localized nor confined in the (111) step planes as narrow as two-atomic-row wide. In case of Cu(755), we still observed the two-dimensional surface state and explained that its wave function can be distributed to the atomic layers under the neighboring terraces. For Cu(911) there are no atomic layers under the neighboring terraces because the (111) step planes are the steps. There the surface state cannot be delocalized and therefore does not be induced. The third is that the surface state shifts above the Fermi level.

The Second argument is consistent with the difference in the surface state of Ni(755) and Cu(755). As stated in the introduction section, on Ni(755) we found one-dimensional step state while there is no such state on Cu(755). We explained that the difference is due to the contribution of the *d* bands. Since the *d* bands overlaps the *sp* surface state just below the Fermi level in the Ni valence band, the *d* bands have considerable contribution on the *sp* surface state and introduce localized nature into the *sp* surface state. Without the contribution of the *d* band about 2 eV away from the Fermi level, there is no step state induced on Cu(755).

The several experimental results support the third argument. On stepped Cu surfaces vicinal to (111), the energy shift of the surface-state band is observed and the energy shifts of surface-band bottom are shown to be proportional to the inverse square of terrace width L^{-2}[4,5,9]. The dependence of the surface-band energy shift on the inverse square of terrace width is shown in Fig. 7. Regardless of the difference in surface structure, we can estimate the possible shift for Cu(911) from its terrace width. The

Fig. 7. The dependence of the shift in the maximum binging energy of *sp* surface state on several stepped Cu surfaces on the inverse square of their terrace widths.

energy of the surface-band bottom for Cu(911) is estimated to be 2.8 eV well above the Fermi level. So an inverse-photoemission- and scanning-tunnelling-spectroscopy
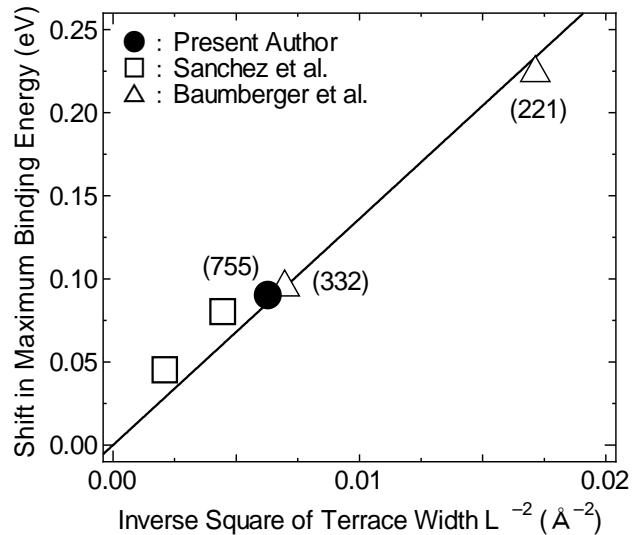
investigations may settle this problem.   We believe tentatively that the last argument may be most probable.

Summary

We performed a SR-ARUPS investigation on stepped Cu(911) in the expectation of creating a new surface material with new one-dimensional surface states.   Since Cu(911) has (111) planes as steps, we expected that (111)-derived *sp* surface state is induced just as on planar Cu(111) and that the surface state has one-dimensional nature being localized at steps.   In SR-ARUPS spectra, however, we observed only a single peak whose dispersion revealed to be the bulk *sp*-band peak and so there induced no new surface state on Cu(911).   The reason for this is discussed and is concluded to be most probably an energy shift of the surface state above the Fermi level.

References

[1] F. Reinert, G. Nicolay, S. Schmidt, D. Ehm and S. Hüfner: Phys. Rev. B **63** (2001) 115415.

[2] H. Namba, N. Nakanishi, T. Yamaguchi, T. Ohta and H. Kuroda: Surf. Sci. **357-358** (1996) 238.

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

[4] K. Ogawa, K. Nakanishi, H. Namba: Solid State Communications **125** (2003) 517.

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

[6] H. Namba, M. Obara, D. Kawakami, T. Nishimura, Y. Yan, A. Yaghishita and Y. Kido: J. Synchrotron Rad. **5** (1998) 557.

[7] H. Iwai, H. Namba, Y. Kido, M. Taguchi and R. Oiwa: J. Synchrotron Rad. **5** (1998) 1020.

[8] C. Baldacchini, *et. al.*: Phys. Rev. B **68** (2003) 195109.

[9] O. Sánchez,   *et. al.*: Phys. Rev. B **52** (1995) 7894.