

One-dimensional Electronic State of Stepped Ni(332) Surface Studied by Angle-Resolved Ultraviolet Photoelectron Spectroscopy at SORIS Beamline (BL-8)

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Abstract

We have investigated the surface electronic structure of stepped Ni(332)[=6(111)×(111)] in the expectation of observing one-dimensional surface state by angle-resolved ultraviolet photoelectron spectroscopy using synchrotron radiation(SR-ARUPS). In SR-ARUPS spectra, we observed two surface-sensitive peaks at ~ 0.5 and ~ 0.1 eV below Fermi level E_F revealed by O₂ adsorption. The former peak disperses downwards away from E_F parallel and perpendicular to the steps, which can be attributed to the (111) terrace-derived two-dimensional surface state. Though the latter peak disperses upwards parallel to the steps, on the other hand, it has almost no dispersion in the perpendicular direction. This flat dispersion is the clear evidence that the peak just below E_F stems from an electronic state localized at the steps. Considering the flat and upwards dispersions perpendicular and parallel to the steps, this step-localized state is concluded to be one-dimensional electronic state.

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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 Ni(111), the surface states have a high in-plane isotropy being two-dimensional[1,2]. 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). 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(7 9 11) which has a regular array of (110) steps, ARUPS spectra revealed that the two-dimensional surface state retains the nature and more importantly that a new anisotropic state is induced[3,4]. The new state on Ni(7 9 11) shows almost flat dispersion perpendicular to the steps. Moreover, alkali metals adsorbed at the steps more sensitively reduced the intensity of the new-state peak than that of the two-dimensional one in the ARUPS spectra. So the new state was concluded to localize at the steps. Similarly one-dimensional step state is found at (100) steps on Ni(755)[5]

These results pose an important question about how the step-localized states are induced on the stepped surfaces. One possibility is that we observe surface states only on (110) and (100) steps. The other is whether a termination of in-plane periodicity at the steps induces the step-localized states just as surface states on planar surfaces. The former is partially denied since we observe the step states both on Ni(7 9 11) and Ni(755). Possibly, therefore, there is no step dependency. By observing the step state on Ni stepped surfaces with (111) steps, we can conclusively confirm this point. We note here that because on such Ni stepped surfaces both steps and terraces have the (111) surfaces and thus the same symmetry, a step state and a terrace state may couple into one surface state.

In order to clarify these points, in the present study, we determined to investigate the surface state on Ni(332) whose step is (111) different from Ni(7 9 11) and Ni(755). We report in the following sections of the present paper the results of ARUPS measurement on Ni(332) using synchrotron radiation for excitation.

Experimental

Ni(332)[=6(111)×(111)] is inclined by 10.02° with respect to (111) towards $[1\bar{1}2]$ (Fig. 1). The calculated average terrace width is 11.5 \AA . The step direction is along the $[\bar{1}10]$ direction. The samples were cut from a (111)-oriented single-crystal rod and polished mechanically. We cleaned the samples by repeated cycles of Ar^+ ion sputtering at 0.5 keV and annealing at 1080 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).

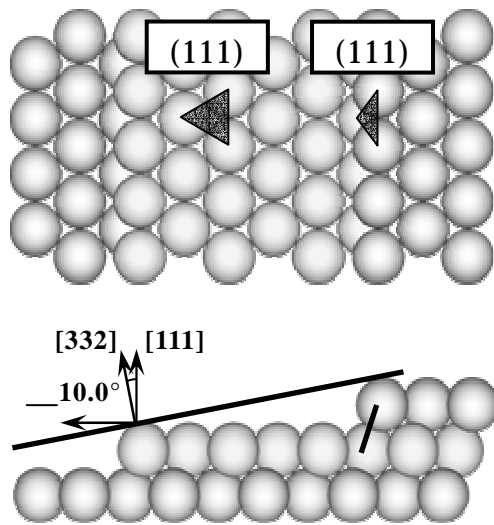


Fig. 1. Ball model of Ni(332) stepped surfaces.

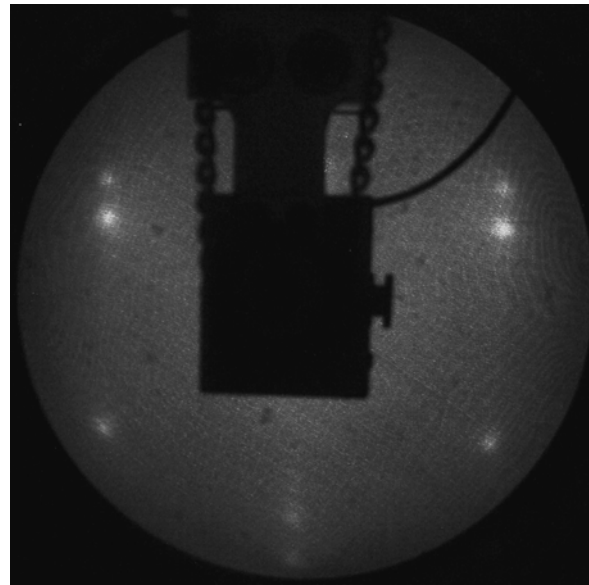


Fig. 2. LEED pattern from stepped Ni(332) at $E_k = 118 \text{ eV}$.

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 $\pm 2^\circ$. 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 $|55^\circ - \theta_e|$ and varied with θ_e , where θ_e is the emission angle measured from $[111]$. The azimuth angle is changed also by rotating samples around the terrace normal of $[111]$ 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 Ni(332) taken around the $\bar{\Gamma}$ point of the surface Brillouin zone at $h\nu=10$ eV in (a) the parallel and (b) 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 Ni(111) is observed.

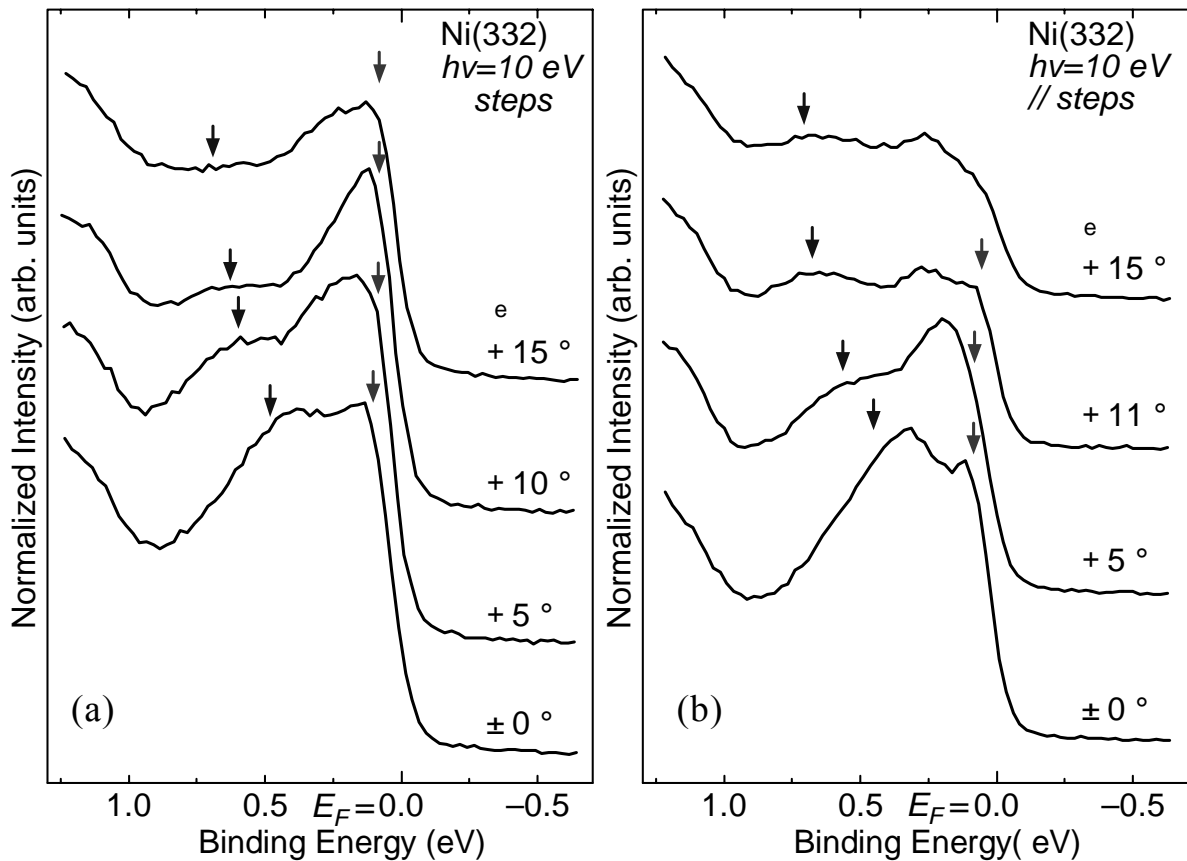


Fig. 3. ARUPS spectra taken at $h\nu=10$ eV in (a) the perpendicular and (b) parallel configurations on stepped Ni(332). The arrows indicate the position of surface-sensitive peaks revealed by O_2 adsorption below.

In Fig. 3 we observed a single broad peak with some structure from bulk and surface components. In order to extract surface components from the spectra we adsorbed O_2 on Ni(332) since surface components are very sensitive to the condition of the surface and decrease its peak intensity upon surface contamination more rapidly than bulk components. Figure 4(a) shows the change in the spectra taken at the emission angle of $+10^\circ$ in the perpendicular configuration upon O_2 adsorption at various exposures. The change is clearer in the difference (Adsorbed - Clean) spectra in Fig. 4(b). Upon O_2 adsorption one can see two peaks at ~ 0.7 and ~ 0.1 eV below Fermi level E_F decreased their intensity rapidly, revealing that these peaks are surface component.

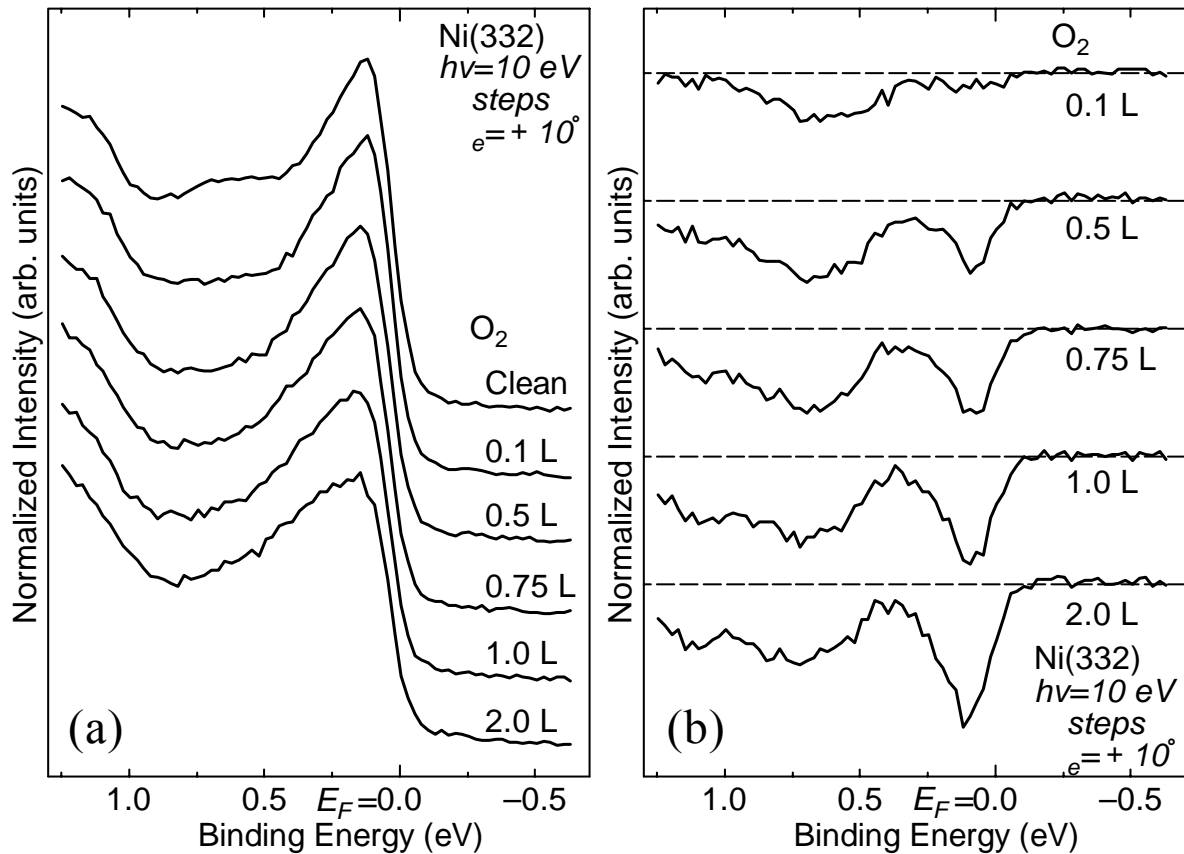


Fig. 4. ARUPS spectra taken at $h\nu=10$ eV in (a) the parallel configuration after O_2 adsorption at several exposures on stepped Ni(332) and (b) the difference (Adsorbed-Clean) spectra.

The difference spectra at all observed emission angles of photoelectron are collected in Fig. 5. We can see that the peak at higher binding energy disperses downwards away from ~ 0.5 eV at the $\bar{\Gamma}$ point in both the parallel and perpendicular configurations. This isotropic dispersion is very similar to the surface state on planar Ni(111) and thus the peak at the higher binding energy is assigned to be the (111) terrace-derived surface state. On the other hand, the peak just below E_F disperses anisotropically. The peak shows almost flat dispersion perpendicular to the steps, whereas in the parallel configuration the peak slightly disperses upwards. This flat dispersion perpendicular to the steps is the clear evidence that this electronic state is localized at the steps and that there is almost no interaction between the steps. The finite dispersion parallel to the steps indicates that the electronic state is one-dimensional.

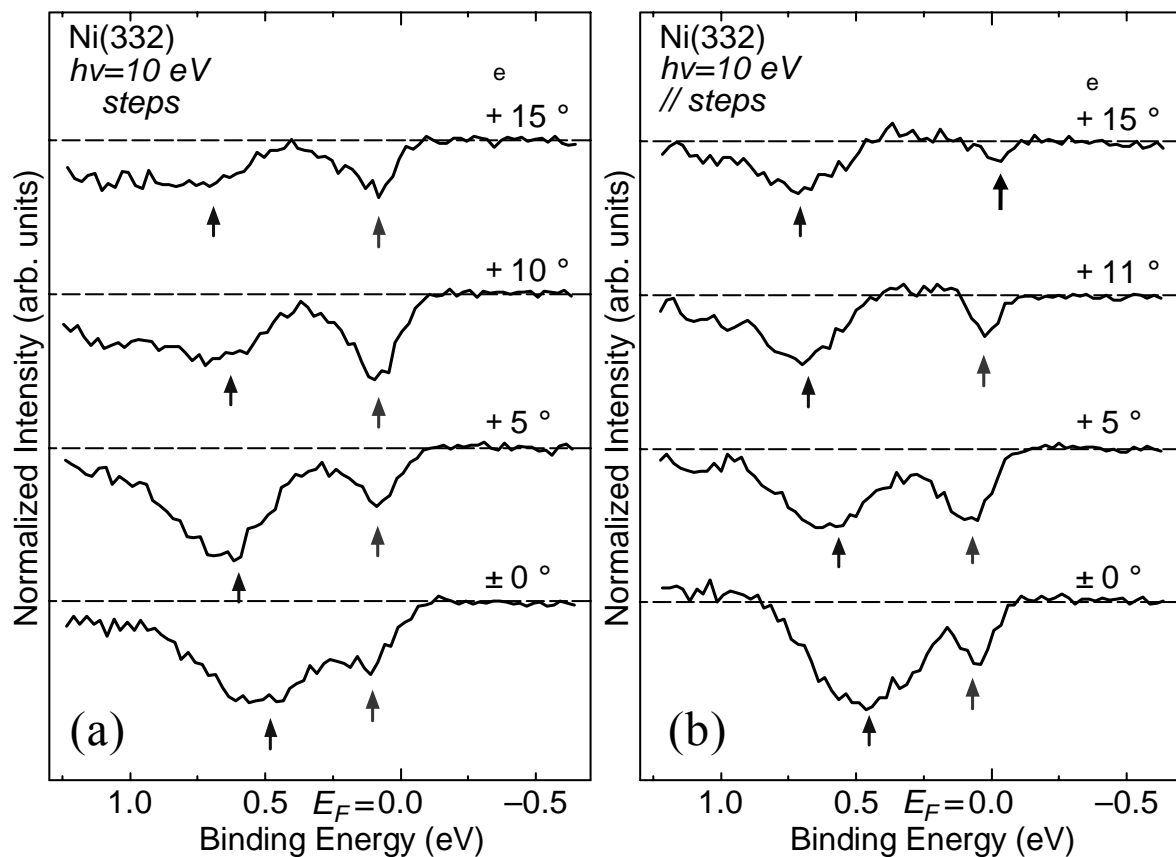


Fig. 5. Difference (Adsorbed-Clean) spectra taken at $h\nu=10$ eV in the (a) perpendicular and (b) parallel configurations after O_2 adsorption of 1.0 L on stepped Ni(332). The arrows indicate the position of surface-sensitive peaks revealed by O_2 adsorption.

As in the preceding sections, we observed one-dimensional state of surface origin localized at the steps in the ARUPS spectra of stepped Ni(332). Therefore the step-localized states are found on Ni(7 9 11), Ni(755) and Ni(332). Since these three stepped surfaces have different type of steps, namely (110), (100) and (111), we can suppose that the step states are independent of step type. Rather the existence of steps is necessary for inducing the step states. More concretely, we can say that the termination of in-plane periodicity due to the steps induces the step-localized states just as surface states on planer surfaces.

Another consequence of observing the step state on Ni(332) is that the terrace and step states do not couple into one surface state even though the steps and terraces have the same symmetry. This might be because the step and terrace states are slightly separated in binding energy. More possibly, the type of these states may be different. Since the downward dispersion of the terrace state closely traces the one of bulk d band, the terrace state must have considerable contribution from the d band. On the other hand, the step state disperses upwards parallel to the steps. So the direction of dispersion is opposite with each other. The upward dispersion of the step state might be an indication of s - p character, which similarly disperses upwards. The difference in character of the states would spoil the interaction between them and hinder them to couple.

Summary

We have investigated the surface electronic structure of stepped Ni(332) in the expectation of observing one-dimensional surface state by SR-ARUPS. In SR-ARUPS spectra, we observed two surface-sensitive peaks at ~ 0.5 and ~ 0.1 eV below Fermi level E_F revealed by O_2 adsorption. The former peak disperses downwards away from E_F , parallel and perpendicular to the steps, which can be attributed to the (111) terrace-derived two-dimensional surface state. Though the latter peak disperses upwards parallel to the steps, on the other hand, it has almost flat dispersion in the perpendicular direction. This flat dispersion is the clear evidence that the peak just below E_F stems from an electronic state localized at the steps. Considering the flat and upwards dispersions perpendicular and parallel to the steps, this step-localized state is concluded to be one-dimensional electronic state.

The observation of the step states on Ni(7 9 11), Ni(755) and Ni(332) leads us to a conclusion that the termination of in-plane periodicity due to the steps induces the step-localized states just as surface states on planer surfaces.

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