Potassium-induced Electronic State on Stepped Ni(755) Surface Studied by Angle-Resolved Ultraviolet Photoelectron Spectroscopy at SORIS Beamline (BL-8)

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Abstract

We have fabricated one-dimensional(1D) potassium chains on stepped Ni(755) [=6(111)×(100)] and have investigated the atomic and electronic structures by means of low energy electron diffraction(LEED) analysis and angle-resolved ultraviolet photoelectron spectroscopy using synchrotron radiation(SR-ARUPS) with the expectation of observing 1D free-electronic-like electronic state. From the comparison between the observed and the kinematically calculated LEED patterns we concluded that potassium adsorbates form 1D 2× periodic atomic chains on Ni(755) at around 0.09 monolayer of potassium. SR-ARUPS spectra taken at the SORIS beamline reveal a potassium-induced electronic state.

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Introduction

The study of one-dimensional(1D) electronic states is very important as one of the topics in physics since 1D states exhibit many interesting phenomena like Peierls transition, charge density wave, non-Fermi Liquid behaviors such as disappearance of Fermi surfaces, and so on. Due to the difficulty in growing high-quality single crystals in general, the study of 1D electronic states was limited to organic materials with very high anisotropy like TTF-TCNQ[1] in the past. At present, one can fabricate a great variety of low-dimensional structures including 1D structures on surfaces of matters and so can avoid this difficulty. Among them, Namba *et al.* made stepped surfaces of metals as Ni(7 9 11) and Ni(755) and proved that the 1D steps with monatomic height on these two surfaces form 1D surface electronic states localized at the steps by means of angle-resolved ultraviolet photoelectron spectroscopy using synchrotron radiation(SR-ARUPS)[2-4].

These stepped surfaces are very interesting not only for their native 1D electronic states. On the stepped surfaces one can fabricate ultimate 1D structures, atomic chains, because step edges trap adsorbates more preferentially than terraces (so-called step decoration). These atomic chains must have 1D electronic states because of their 1D structure. Since we wanted to study simple and fundamental, that is, free-electron-like 1D electronic states as the first step, we decided to grow atomic chains of alkali metals whose valence bands are composed of *s* electrons by the step decoration method using Ni(755) as a template. In the present paper, we report that 1D atomic chains of potassium are successfully obtained on Ni(755) as revealed from a close comparison between the kinematically calculated and the observed low-energy-electron-diffraction (LEED) patterns and that a potassium-induced electronic state is observed by SR-ARUPS.

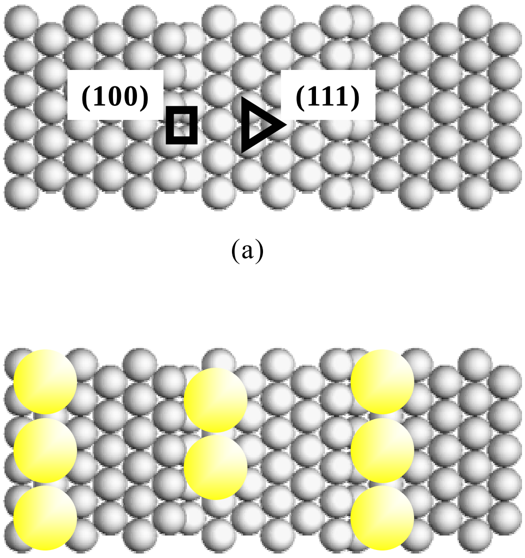

Fig. 1. Ball model of (a) Ni(755) and
(b) 0.09-ML potassium/Ni(755).

Experimental

As in Fig. 1(a), Ni(755) stepped surface [=6(111)×(100)] is inclined by 9.5° with respect to (111) towards [2-1-1]. The nominal terrace width is 12.2 Å. The straight steps with monatomic height run along the [01-1] direction. The Ni(755) sample was 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 about 1030 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 LEED patterns.

It is well-known that potassium adsorbates form a $p(2\times2)$ hexagonal structure on planar Ni(111) at the coverage of about 0.25 ML(monolayer)[5-8]. This is because on-top sites are preferred adsorption sites and the stable nearest-neighbor distance of potassium is about twice as much as that of nickel. So, we suppose at the beginning that the nearest-neighbor distance of potassium in complete atomic chains is also twice as much as that of and nickel (See Fig. 1(b)). We, then, deposited potassium at the coverages around 0.09 ML which amounts to complete 2× periodic atomic chains.

Deposition of potassium is from a commercial dispenser (SAES getter) after careful degassing. The deposition rate is estimated to be ~1 mML/s by means of a quartz crystal oscillator. We controlled the amount of deposited potassium by deposition time from opening to closing a shutter in front of the SAES getter. Typical pressure during potassium deposition is kept to be below 5×10^{-10} Torr using a liquid-nitrogen shroud surrounding the SAES getter. We, then, analyzed the surface structure of potassium on Ni(755) by LEED as in the following section.

Measurements of SR-ARUPS were carried out at the SORIS Beamline(BL-8), a compact VUV beamline for high-resolution photoelectron spectroscopy at the SR Center, Ritsumeikan University[9]. 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[10]. The total energy resolution of the monochromator and the energy analyzer was estimated to be about 35 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.

Results and discussion

Figures 2 and 3 show the observed and the calculated LEED pattern for both clean Ni(755) and 2× potassium chains on Ni(755) based on a kinematical calculation[11]. In the figures, the steps run horizontally and the vertically downward direction is [-211]. We checked the validity of the calculation by comparing the observed and the calculated LEED pattern for clean Ni(755). When we optimized the inner potential and relaxation, we could properly reproduce the split-spot LEED pattern as indicated in Fig. 2.

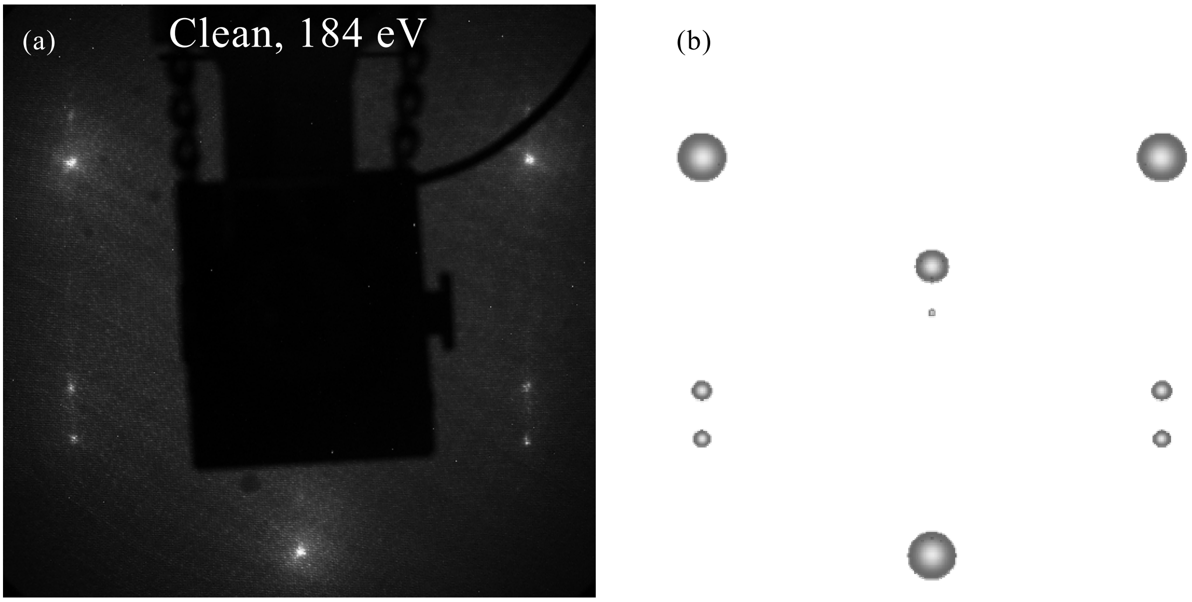

Fig. 2. (a) Observed and (b) kinematically calculated LEED patterns for bare stepped Ni(755).

Figures 3(a) shows a LEED pattern observed for K-adsorbed surfaces of Ni(755) at the primary energy of 178 eV. Upon the deposition of 0.09 ML of potassium the doubly split spots from the Ni(755) substrate remain unchanged, though the background became relatively brighter. This is a clear evidence showing that the substrate did not reconstruct upon potassium deposition significantly and retain the original stepped structure. Therefore, any additional features in these LEED patterns can be attributed to the structure of adsorbed potassium.

In Fig. 3(a), short streaks can be found on K/Ni(755) as indicated by thin and thick arrows. The thin arrows indicate the streaks of 1× periodicity, and the thick arrows the streaks of 2× periodicity. The 2× streaks clearly indicate that the potassium adsorbates form 2× atomic chains as we expected. The observation of short streaks, however, needs a little more explanation since ideal atomic chains only give rows of dots rather than streaks as in Fig. 3(b).

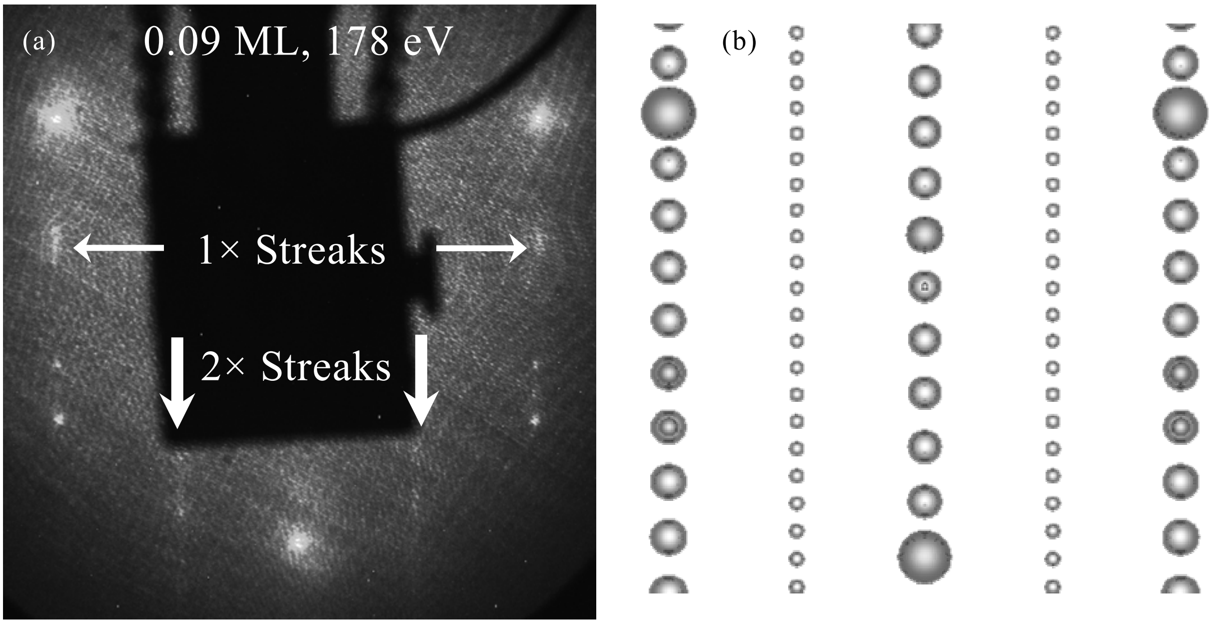

Fig. 3. (a) Observed and (b) kinematically calculated LEED patterns for 0.09-ML K on Ni(755).

Intuitively a single 1D atomic chain can give streaks. However, the growth of only a single chain is unreasonable. Alternatively, short chains at lower coverages also can give streaks, this time with not 2× but 1× periodicity because of the randomness in position of chains. So we believe that the potassium atomic chains grow as in the following. At very low coverages, potassium adsorbates diffuse somehow and meet other adsorbates, forming short chains. So 1× long streaks are expected in the LEED pattern, which we indeed observed (not shown). With the further increase in coverage, the atomic chains become longer and correspondingly the streaks become shorter. Just before the coverage of 0.09 ML 2× streaks appear together with 1× streaks, which is just the LEED pattern in Fig. 3(b).

Figure 4 is the photoemission and difference spectra on Ni(755) with various potassium coverages taken around the $\bar{\Gamma}$ point of the surface Brillouin zone at $h\nu$=24 eV. The abscissa is the binding energy and the ordinate the intensity normalized by the Ni bulk peak intensity at ~1.3 eV. The photon energy of 24 eV was adopted since bulk potassium shows the stronger intensity at that photon energy[12].

In Fig. 4, we observed two strong peaks at ~0.6 and ~1.3 eV on bare Ni(755). Upon deposition of potassium a new peak evolves as a shoulder at ~0.1 eV. In difference spectra (absorbed-bare), the peak is much easier to recognize. We plotted the areal intensity against potassium coverage in Fig. 5. We can see that the intensity gets stronger with the increase in potassium coverage and therefore safely assigned the peak is induced by potassium adsorbates.

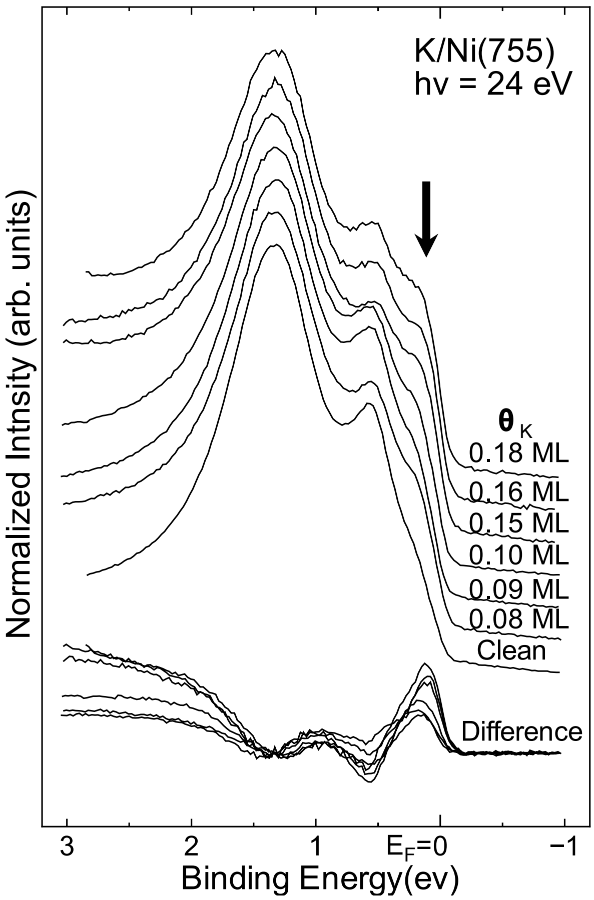

Fig. 4. ARUPS spectra taken at *hv*=24 eV at various potassium coverages on stepped Ni(755) and the difference (Adsorbed-Clean) spectra.

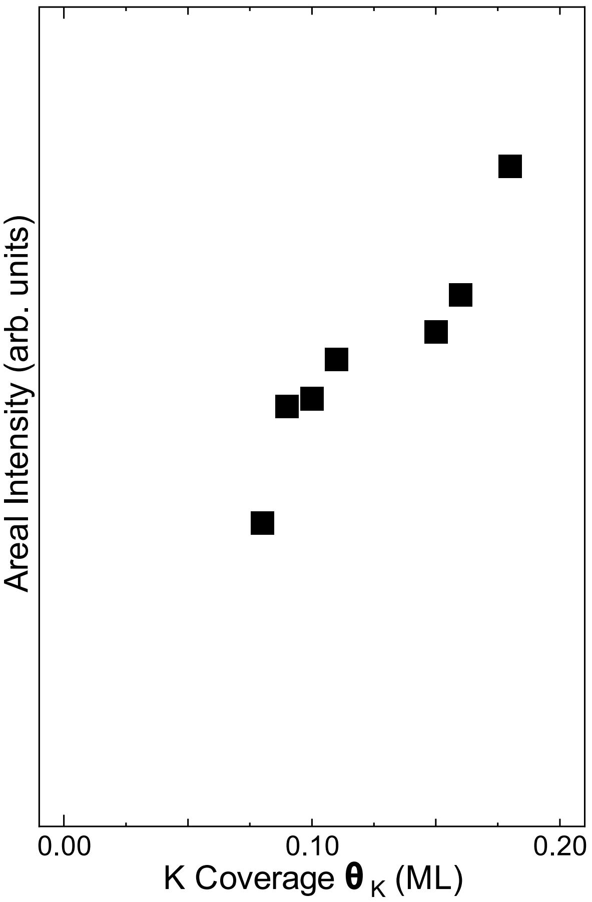

Fig. 5. Areal intensity of K-derived peaks at ~0.1 eV in ARUPS spectra in Fig. 4.

Since potassium has 4*s* electrons as valence electron, we might be able to attribute the peak at ~0.1 eV to K 4*s* state. However, we suppose that we have to be more careful in doing so because of the following reasons. When we look the difference spectra in Fig. 4 more closely, we notice that the peak is slightly shifted towards the lower binding energy as the coverage increases. This shift is opposite with the established model of alkali adsorption on metals. Aruga *et al.* reported that the K 4*s* state on Cu(100) shifts toward the higher binding energy with the increase in potassium coverage by electron energy loss spectroscopy[13]. This is because potassium adsorbates, which are rather ionic at low coverages, become more metallic gaining back electrons from the substrate (so-called back donation). Accordingly, the areal intensity of the K-derived peak should increase almost linearly at the low coverages and enhance more at higher coverages, which is not so clear in Fig. 5. So we believe that we still need to determine, for example, the energy dispersion and symmetry of that peak in order to clarify the origin of the potassium-induced peak.

Summary

We fabricated 1D potassium chains on stepped Ni(755) and investigated the atomic and electronic structures by means of LEED and SR-ARUPS. From the comparison between the observed and the kinematically calculated LEED patterns we concluded that potassium adsorbates form 1D 2× periodic atomic chains on Ni(755). SR-ARUPS spectra taken at the SORIS beamline reveal a potassium-induced electronic state.

As future works, we need the determination of energy dispersion and symmetry of that peak in order to clarify the origin of the potassium-induced peak.

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