One-dimensional Atomic and Electronic Structures of Submonolayer Potassium Deposited on Stepped Surface of Ni(755)

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Abstract

On stepped surface of Ni(755)[=6(111)×(100)] we deposited 0.01~0.16 ML (monolayer) of potassium aiming to fabricate one-dimensional(1D) potassium atomic-chain structure and to understand its growth process by observing the low-energy-electron-diffraction(LEED) patterns. The LEED patterns which can be attributed to potassium adsorbates show a distinct dependence on potassium coverage that 1× streaks first appeared at low coverages up to 0.04 ML and later 2× streaks appeared at about 0.09 ML. The streaks become like spots at the higher coverage. These coverage-dependent changes in LEED patterns could be explained in a close comparison with kinematically calculated LEED patterns constructing a reasonable growth model.

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1. Introduction

In low-dimensional physics, one-dimensional (1D) electronic states are one of the most fascinating topics since they exhibit many interesting phenomena. They are, for instance, charge density wave, Peierls transition, non-Fermi Liquid behaviors such as disappearance of Fermi surfaces, and etc. Since the surfaces can provide a variety of structures and thus opportunities for the study of 1D electronic states, a trend to study such 1D electronic states on the "surfaces" of matters is growing recently[1-7]. Among them, Namba *et al.* showed for the first time that stepped surfaces of Ni(7 9 11) and Ni(755) induce native zero-dimensional (0D) and 1D electronic states localized at the steps, respectively[1, 3, 4]. In addition to these native localized electronic states, on these stepped surfaces of metals one can also fabricate ultimate 1D structures, atomic chains, because of preferential adsorption on the steps more than on terraces (so-called step decoration). The 1D structure of these atomic chains must lead to 1D electronic states.

In terms of atomic chains we previously fabricated atomic chains of alkali metals aiming free-electron-like 1D electronic states by the step decoration method using Cu(755) and Ni(755) as templates[7]. Figure 1 is the ball model of the (755) stepped surface. The (755) surface [=6(111)×(100)] is inclined by 9.5° from the (111) terraces towards [2-1-1]. The straight steps with monatomic height run along the [01-1] direction. The nearest-neighbor distance of potassium in complete atomic chains should be about twice as much as those of nickel and copper because the stable nearest-neighbor distance of potassium is almost twice as much as those of nickel and copper on their (111) surfaces[8, 9]. We, then, evaporated potassium at the coverage of 0.09 ML(monolayer). We define one ML as the atomic density of the substrate atom, that is one potassium atom per one substrate atom. 0.09 ML amounts to complete 2× periodic atomic chains on each step. At 0.09 ML coverage, low-energy-electron-diffraction (LEED) pattern for K/Ni(755) alone shows 1× and 2× streaks which indicates the formation of 2× potassium atomic chains. Therefore we concluded that 1D atomic chains of potassium are successfully fabricated only on Ni(755) but not on Cu(755).

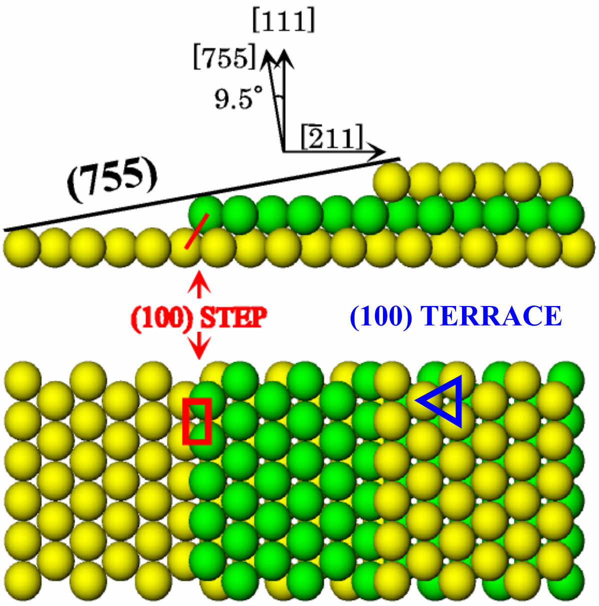

Fig. 1. The hard-sphere model of stepped Ni(755) (Upper, side view; bottom, top view). The angle between the (755) and (111) surfaces is 9.5°. The terraces consist of 6-row wide (111) and the steps (100). The nominal terrace width is 12.2 Å.

The growth process of 1D potassium chains must be known to clarify the reason why 1D potassium chains form only on Ni(755). Moreover, the details of the growth process will contribute to diversified fabrication of other 1D atomic chains and hence to the development of physics in one dimension. In the present study, we deposited submonolayer potassium on Ni(755) and analyzed LEED patterns at various coverages. We also attempted a preliminary investigation of the electronic structure of 1D potassium chains by means of angle-resolved ultraviolet photoelectron spectroscopy using synchrotron radiation (SR-ARUPS).

2. Experimental

Only a short explanation of the procedure for sample preparation is given here since explained in detail elsewhere[7]. We first cut the Ni(755) substrate from a (111)-oriented monocrystalline rod (its diameter is 8 mm), and polished it mechanically. Second, the substrate was cleaned by repeated cycles of Ar^+ ion sputtering at ≤ 1 keV and annealing in a sample-preparation chamber whose base pressure is as below as 1×10^{-10} Torr. The annealing temperature is about 1070 K. Final confirmation of the surface cleanliness and crystallinity of the substrate was done by Auger electron spectroscopy (AES) and LEED patterns.

We deposited potassium at various submonolayer coverages at room temperature on the Ni(755) stepped substrate from a carefully degassed commercial dispenser (SAES getter). We estimated that the deposition rate is about 1 mML/s from a quartz crystal oscillator. The potassium coverage was controlled by deposition time from opening to closing a shutter in front of the SAES getter. Using a liquid-nitrogen shroud surrounding the SAES getter the pressure in the preparation chamber was kept below 5×10^{-10} Torr even during the potassium deposition. AES spectra measured just after the deposition shows no contamination peaks from other than substrate materials and potassium. Finally the surface structure of potassium on Ni(755) was analyzed by observing LEED patterns and comparing them with calculated ones based on a kinematical calculation[10, 11].

We measured all SR-ARUPS spectra at the SORIS Beamline(BL-8), a compact VUV beamline for high-resolution ultraviolet photoelectron spectroscopy at the SR Center, Ritsumeikan University[12-14]. The total energy resolution of the beamline including the energy analyzer was estimated to be about 35 meV for the present measurements. The angle between the incident p-polarized synchrotron radiation and the axis of the energy analyzer was fixed to be 55°. The acceptance angle of the analyzer for photoelectrons was ±2°.

3. Results

First, we showed LEED patterns observed for K-adsorbed Ni(755) stepped surfaces at various submonolayer coverages from 0.01 to 0.16 ML in Fig. 2(a)-(f). The primary energy is around 180 eV and is given in the parentheses. Strong single and doubly split spots are from the substrate characteristic of stepped Ni(755)[7] and are very recognizable at the lowest coverages. Together with them, relatively weak short streaks indicated by thin and thick arrows can be seen and their presence is demonstrated in Fig. 3 below. Even after the potassium deposition from 0.01 up to 0.16 ML, the doubly split spots from the substrate remain almost unchanged, which shows that the substrate keeps the original stepped structure, though there may be a small relaxation especially for atoms at the steps. Therefore, we assigned any additional features such as the streaks in these LEED patterns as originating from the structure of adsorbed potassium.

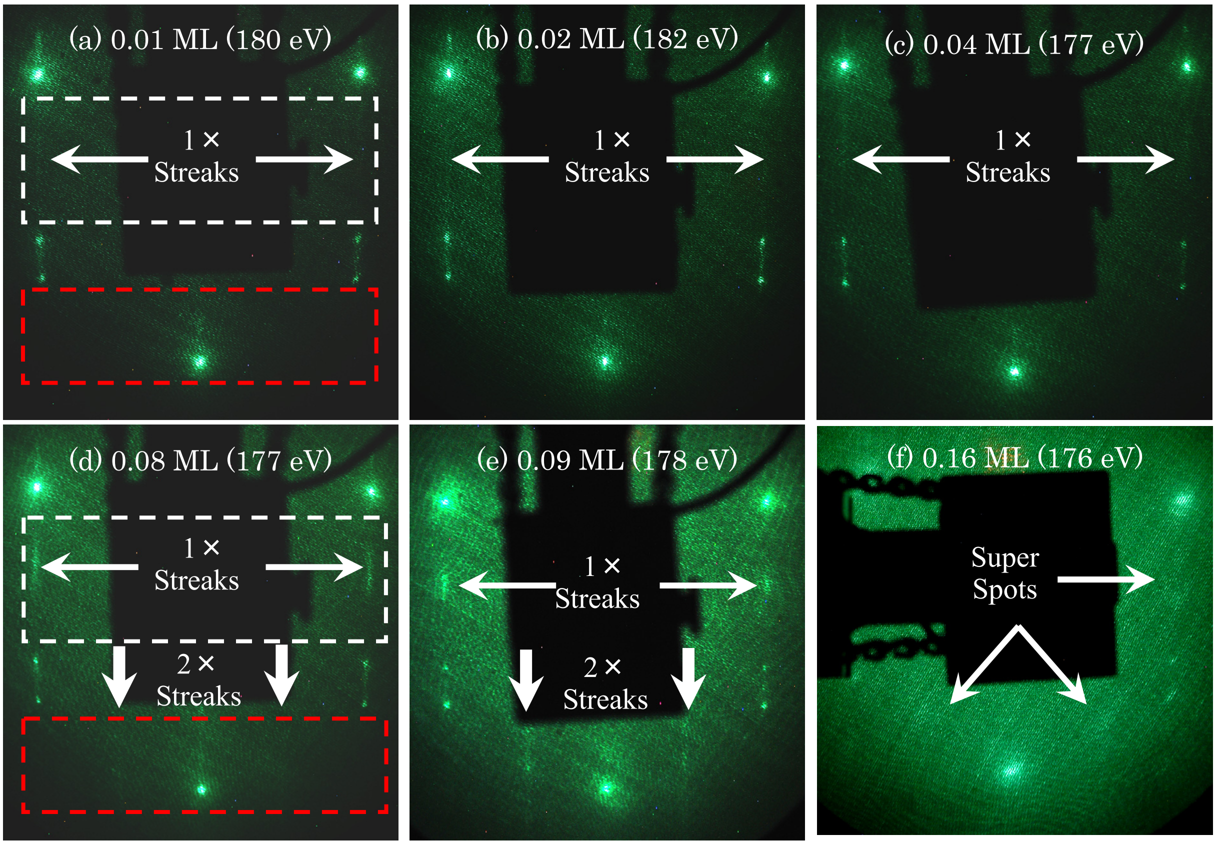

Fig. 2. The experimental LEED patterns observed for 0.01-0.16-ML potassium deposited Ni(755): (a) 0.01 ML; (b) 0.02 ML; (c) 0.04 ML; (d) 0.08 ML; (e) 0.09 ML; (f) 0.16 ML. The primary energy is indicated in parentheses. The steps run horizontally and the vertically downward direction is [2-1-1] in the figure. The intensities within the enclosed regions are integrated vertically into line profiles as shown in Fig. 3 in order to see weak features more clearly and unambiguously.

Here we note a big difference between low and middle coverages for the streaks. On the one hand, only weak 1× periodic streaks indicated by thin arrows are found at the low coverages from 0.01-0.04 ML as Fig. 2(a)-(c) show. On the other hand, Fig. 2(d) and (e) show that 1× streaks become stronger and 2× streaks appear at the middle coverages around 0.09 ML. The streaks become shorter with the further increase in coverage above 0.08 ML and finally spotty at 0.16 ML.

The presence of weak streaks was confirmed as below. The LEED intensities within the enclosed regions in Fig. 2(a) and (d) were vertically integrated into line profiles. In Fig. 3 the thin black line profiles are for the 1× streaks and its center is removed because the manipulator casted shadow. The thick red line profiles are along the 2× streaks. The strong peaks at the center stem from a single spot of the substrate and thus are not considered here. On one hand, even at 0.01 ML 1× streaks are clearly seen and there are no 2× streaks found. On the other hand, 2× streaks appear together with strong 1× streaks at 0.08 ML. We also confirmed the presence of the weak extra spots in the LEED pattern at 0.16 ML in Fig. 2(f) by the same intensity analysis (not shown).

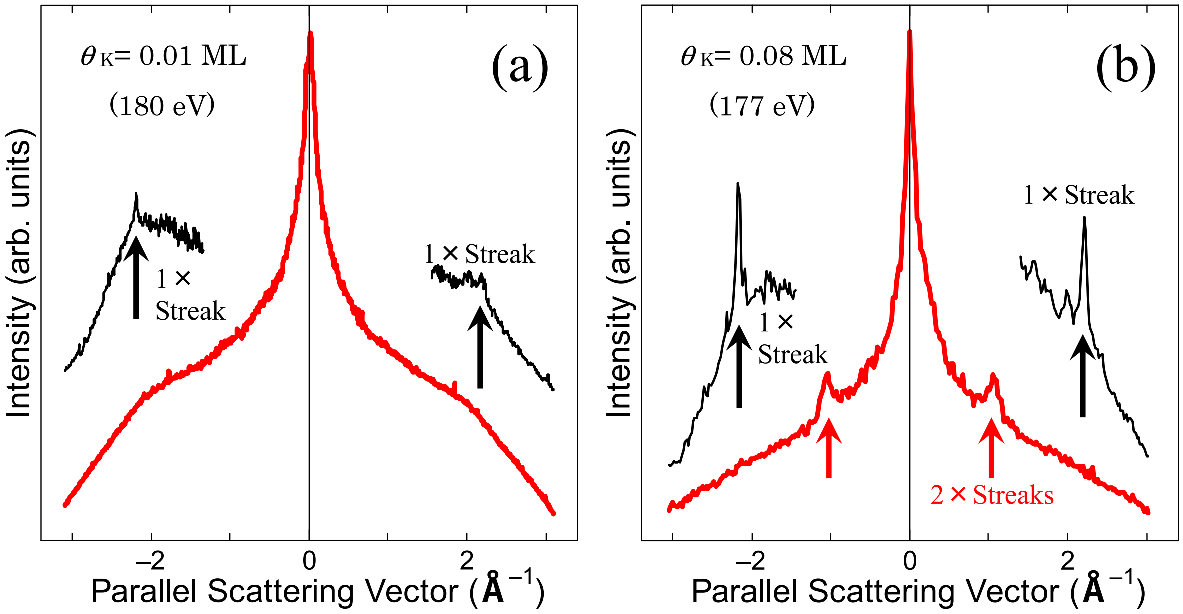

Fig. 3. The line profiles into which intensities of the LEED features within the enclosed regions in Fig. 2(a) and (d) are integrated vertically for (a) 0.01 and (b) 0.08 ML. The thin black line profiles correspond to the upper regions in Fig. 2(a) and (d) and are for the 1× streaks, and its center is removed because shadowed by the manipulator. The thick red line profiles correspond to the lower regions in Fig. 2(a) and (d) and are for the 2× streaks. Single spots from the substrate appear as the strong peak at the center.

4. Discussion

Though the stable nearest-neighbor distance of potassium is almost twice as much as that of nickel[8], we observed only the 1× streaks at the low coverages. We discuss possible reasons for this first and the growth process second.

Contraction of potassium is one of the possible reasons we consider first. As the coverage increases up to 0.5 ML on Ni(111) Chandavarkar reported that the nearest-neighbor separation between potassium adsorbates gets smaller and smaller down to about 4.2 Å[8]. This separation is, however, still greater than that of nickel by about 170%. Moreover, we observed the 1× streaks at much smaller coverages than 0.5 ML. Therefore, the contraction can be safely ruled out.

The second possibility is the ionization of potassium adsorbates. Upon adsorption on Ni(111) and Ni(775) surfaces at low coverages, potassium adsorbates are ionized as revealed by work-function change[15, 16]. Ionic radius of potassium is very smaller than that of metallic potassium[17]. Therefore, ionic potassium might be able to form 1× chains if potassium adsorbates were ionized also on Ni(755). Strong repulsive Coulomb force, however, would keep potassium ions rather separated as Chandavarkar reported[8] and so the ionization makes it more difficult for potassium adsorbates to form 1× chains, although we do not deny the possibility of partial ionization itself.

According to the discussion above, we believe that potassium forms not 1× chains but 2× chains. Then, we have to explain the absence of 2×streaks at the low coverages even from the 2× chains. After evaporation, potassium atoms first get to somewhere on the substrate such as (111) terraces and (100) step edges. Since interaction with Ni(111) is not so strong at room temperature[8], potassium adsorbates on the (111) terraces can diffuse with relative ease. After sufficient diffusion they may be trapped at the (100) step edges because the interaction with potassium adsorbates is stronger than on Ni(111)[7, 8, 18]. Potassium adsorbates might diffuse along the steps to form a small number of 2× atomic chains with only short length inevitably at the low coverages. These scarce short chains at the low coverages such as in Fig. 4(a) give a LEED pattern calculated kinematically in Fig. 4(d).

The validity of the present kinematical calculation which includes the contribution of atomic scattering factor[11] is proved by the properly reproduced split-spot LEED pattern from the Ni(755) substrate indicated by gold spots. The radius of the calculated spots corresponds to the diffracted intensity. For the clarity, the diffracted intensity from potassium adsorbates is enhanced against the substrate. The silver streaks and spots are from potassium adsorbates. In Fig. 4(d) the LEED pattern at low coverages with 1× and much weaker 2× streaks is well-reproduced. One reason for the weakness of the 2× streaks is possibly smaller atomic scattering factor at larger scattering angle. Another and more probable reason is that the apparent periodicity along the steps is 1× since there is no order in the relative positions between the short chains at the same steps and at the different steps.

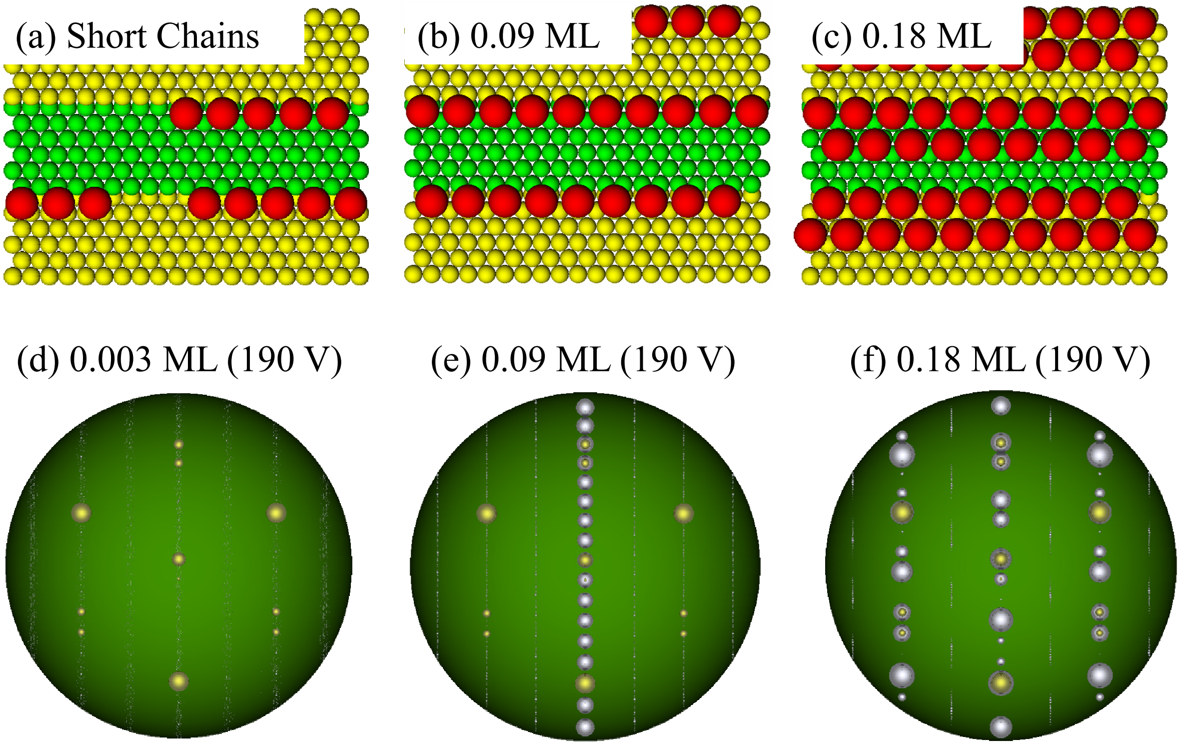

Fig. 4. The hard-sphere models of (a) scarse short chains at low coverages, (b) 2× single-row potassium chains at 0.09 ML and (c) 2× two-row potassium chains at 0.18 ML on Ni(755); (d)-(f) the kinematically calculated LEED patterns for these models[10, 11]. The substrate and potassium adsorbates give the gold and silver spots, respectively. In the figure, the steps run horizontally and the vertically downward direction is [2-1-1] corresponding to the observed ones in Fig. 2.

We here make one note about adsorption site of potassium. Though we depicted the adsorption model in Fig. 4(a)-(c) as if potassium adsorbates sit on the fourfold hollow sites of the (100) steps and the threefold hollow sites of the (111) terraces closest to the steps, there is no strong experimental support. Rather the trap at the fourfold hollow sites may be imperfect. Because if we fix the adsorption site to be only the fourfold hollow sites for example and the trap is perfect, the calculated LEED pattern is not streaky but spotty. This is against the experimental LEED patterns. So potassium adsorbates may sit on other sites along the steps than those sites. Even though the fourfold sites are most stable, the energy gain by sitting at the fourfold hollow sites is not so large at least for the short chains.

This situation is similar for the middle coverages around 0.09 ML. The short streaks are observed in the LEED patterns at 0.08 and 0.09 ML and are well-reproduced in the calculated ones in Fig. 4(e). In the calculation the adsorption site is assumed to be the fourfold hollow sites at the (100) steps and also the middle points between those sites. Only the fourfold hollow sites assumed give spotty calculated LEED pattern, which is again against the experimental LEED patterns.

The streaks become rather spotty at the highest coverage of 0.16 ML. The model shown in Fig. 4(c) could successfully reproduce the observed spotty LEED patterns. In the model potassium adsorbates are assumed to be no longer free along the steps and sit on a certain adsorption site at the steps. Considering reported potassium adsorption on Ni(100)[18], we believe that the site may be the fourfold hollow sites of the (100) steps. With the increase in chain length, only a small energy gain by adsorbing at a weakly stable site may accumulate sufficient to trap the chains. The complete two-row chains model where potassium adsorbates are assumed to sit on the fourfold hollow sites gives the calculated LEED pattern shown in Fig. 4(f), which is in reasonable agreement with the observed one in Fig. 2(f).

The SR-ARUPS spectra for K/Ni(755) at various coverages is shown in Fig. 5. In the photoemission spectra on bare Ni(755) taken around the $\overline{\Gamma}$ point of the surface Brillouin zone at *hv*=24 eV, two strong peaks were observed at ~0.6 and ~1.3 eV. After potassium deposition, a new peak appears as a shoulder at ~0.1 eV. The evolution of the peak can be seen more clearly in the difference spectra plotted at the bottom. The intensity of the peak gets stronger with the increase in θ_K and therefore we could assign the peak is of potassium adsorbates origin. The energy dispersion of this potassium-induced state is to be measured for the determination of dimension in electronic structure and we expect that the dimension must be one-dimensional.

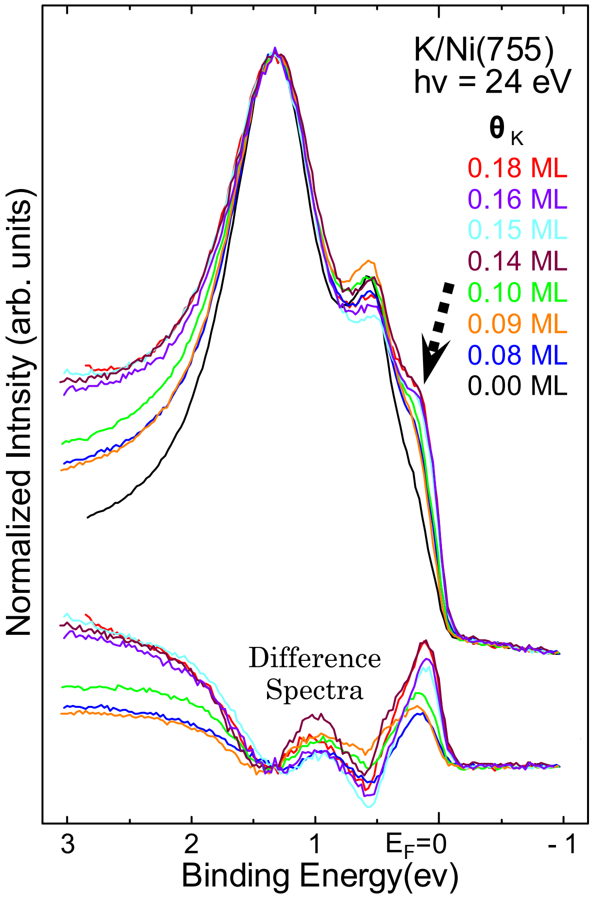

Fig. 5. SR-ARUPS spectra for adsorbed potassium on Ni(755) at various coverages taken at the photon energy of 24 eV around the $\overline{\Gamma}$ point of the surface Brillouin zone. The potassium coverage θ_K is shown in the figure. The dotted arrow indicates the evolved K-induced peak with the increase in θ_K. At the bottom the difference spectra (Clean − K adsorbed) are also plotted.

5. Conclusions

On stepped surface of Ni(755)[=6(111)×(100)] we deposited 0.01~0.16 ML (monolayer) of potassium aiming to fabricate 1D potassium atomic-chain structure and to understand its growth process by observing the LEED patterns. The LEED patterns which can be attributed to potassium adsorbates show a distinct dependence on potassium coverage that 1× streaks first appeared at low coverages up to 0.04 ML and later 2× streaks appeared at about 0.09 ML. From a thorough comparison between the observed and kinematically calculated LEED patterns we suppose the potassium chains grow as follows.

Trapped near the steps potassium adsorbates may be isolated or diffuse along the steps which form only short chains until the low coverages of about 0.04 ML. The LEED patterns tells us that the nearest-neighbor distance of potassium adsorbates within the chains is almost twice as much as those of nickel and that the adsorption site at the steps is not unique at these coverages.

The short atomic chains become longer and turn into single-row chains as the potassium coverage increases. After the completion of the first row, further increase in coverage leads to the growth of the second rows. We believe that at these stages, potassium adsorbates sit on a unique adsorption site probably because a small energy gain by sitting on weakly stable sites may accumulate enough to trap the chains. The candidate site is the fourfold hollow sites at the (100) steps because of the strong interaction with potassium adsorbates[18].

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