Electronic States Localized at Step Edges on Ni(7 9 11) Surfaces Studied by Angle-Resolved Photoelectron Spectroscopy

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Electronic states of Ni(7 9 11) surfaces were studied by angle-resolved ultraviolet photoelectron spectroscopy using synchrotron radiation. The existence of a surface electronic state characteristic of the step and one associated with the terrace is shown from studies of the effect of alkali metal adsorption and the polarization dependence of photoelectron spectra.

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Electronic states of plane surfaces of metal single crystals have been extensively investigated by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). The existence of surface electronic states with two-dimensional nature on those surfaces has been revealed through studies of photon energy dependence and angular distribution of photoelectron spectra [1]. On a stepped surface of a metal crystal, there are periodical rows of monatomic steps or kinks separated by terrace planes. One could expect the formation of some new electronic states localized at step edges. Such electronic states might exhibit more or less one-dimensional character. Although ARUPS experiments were carried out on stepped metal surfaces, experimental identification of the electronic state specific to steps has been unsuccessful so far [2-5]. Therefore it is widely believed that no specific electronic state exists at steps possibly because of the delocalization of electrons in metals. However, there is the possibility that the photoelectron signals due to step electronic states overlap those of the bulk and terrace electronic states, and are hard to separate from the latter in the ARUPS experiments utilizing an inert-gas discharge lamp as the stimulating light. When the synchrotron radiation (SR) is used, one could obtain much information by tuning the photon energy of stimulating light and by changing the polarization direction. In this Letter, we report the results obtained by ARUPS experiments utilizing SR on a $\mathrm{Ni}(7\,9\,11)=5(111)\times(\bar{1}01)$ stepped surface and its alkali-adsorbed states. We have found for the first time evidence for the existence of new electronic states localized at step edges [6].

Experiments were carried out by use of an ARUPS apparatus based on beam line ADES 400 (VG Scientific) at BL7-B [7] in Photon Factory, National Laboratory for High Energy Physics by using linearly polarized radiations in the photon energy range from 5 to 50 eV, the base pressure of the apparatus being under 1×10^{-8} Pa. Samples of Ni(7 9 11) were obtained by spark cutting a Ni single crystal rod (Johnson Matthey, 5N). Sample surfaces were first polished mechanically and electrochemically in air and then cleaned by repeated cycles of Ar^{+} sputtering and annealing at 800 °C within the experimental apparatus. It was confirmed by means of the incident energy dependence of the LEED pattern that, on the clean surface, the periodical rows of monatomic steps expected for Ni(7 9 11) surfaces were arranged along $[\bar{1}2\bar{1}]$ as illustrated in Fig. 1. The geometry of ARUPS measurements is also shown in Fig. 1. The electric vector of incident light and the direction of detecting photoelectrons are in a plane perpendicular to the running direction of the steps. In the present study, the incident angle of stimulating radiation, θ_i, measured from [111] which is normal to the terrace plane, was fixed at 85.8° in *p*-polarization experiments and at 28.8° in *s*-polarization experiments. The angle of photoelectron detection, θ_e, is measured as illustrated in Fig. 1.

Adsorption of alkali metal onto a sample surface was performed by heating an alkali metal dispenser (SAES Getter). Both in Na adsorption and in Li adsorption, LEED patterns remained to show only the double spots characteristic of Ni(7 9 11) up to the saturation coverage, with no extra LEED spot being observed. The alkali metal adsorption resulted in only an increase of the background intensity. These facts indicate that alkali metal atoms are randomly adsorbed on Ni(7 9 11) without causing any surface reconstruction [8].

Figure 2(a) shows the energy distribution curve (EDC)

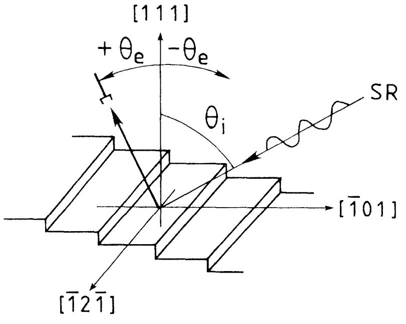

FIG. 1. Ni(7 9 11) stepped surface and geometry of ARUPS measurements. θ_i: incident angle of SR; θ_e: detection angle of photoelectrons. The sign of θ_e is denoted as shown in the figure.

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of photoelectrons measured on the clean surface by stimulating with 10 eV photons in p polarization with $\theta_i = 85.8°$ and $\theta_e = 0°$, together with the corresponding EDC of the state where 0.38 monolayer (ML) of Na has been adsorbed on the surface. The energy position of the Fermi level was determined by use of the EDC of a clean polycrystalline Au sample. The EDC of a clean Ni(7 9 11) surface shows a broad peak (B_1) with the maximum at -1.6 eV measured from the Fermi level and a peak (S_t) at about -0.3 eV with a shoulder (S_s) just below the Fermi level. As can be seen in Fig. 2(a), the intensity of the S_t peak markedly decreases on adsorbing a small amount of Na while the intensity of the B_1 peak is little affected by the Na adsorption. A similar change of EDC was observed also for Li adsorption as we will show later. We found also that intensity reduction can be caused by the adsorption of oxygen that is often used to quench surface electronic states [9]. All these facts suggest that the photoelectron band in the region of S_s and S_t is associated mainly with some surface electronic states which can be easily quenched by alkali adsorption while the B_1 peak is associated with bulk electronic states. From the difference curve shown at the lower part of Fig. 2(a), where we can clearly see the S_s peak, the peak position can be found to be -0.05 and -0.35 eV for S_s and S_t, respectively.

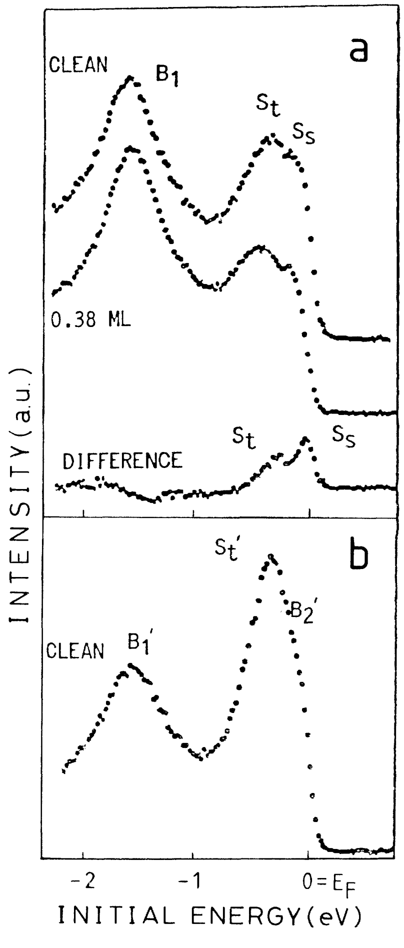

FIG. 2. (a) EDC of a clean Ni(7 9 11) and that after Na adsorption at 0.38 ML coverage; the data are obtained for p polarization at photon energy = 10 eV, $\theta_i = 85.8°$, $\theta_e = 0°$. The difference between the two EDC's is shown at the bottom. (b) EDC of a clean Ni(111) surface for p polarization (photon energy = 10 eV, $\theta_i = 85.8°$, $\theta_e = 0°$).

Since the terrace plane of Ni(7 9 11) has an atomic arrangement similar to Ni(111), it is worthwhile to compare the EDC between these two Ni surfaces in order to elucidate the characters of the photoelectron peaks in the EDC of Ni(7 9 11). We measured the EDC of a clean Ni(111) surface employing the same experimental condition as that used for obtaining the EDC of Ni(7 9 11). The result is given in Fig. 2(b), which shows a broad peak (B_1') at about -1.6 eV from the Fermi level and a stronger peak (S_t') at about -0.4 eV with a weak shoulder (B_2') near the Fermi level. On Ni(111), ARUPS studies were carried out by Himpsel and co-workers [10,11], who assigned the B_1' and B_2' peaks of Ni(111) to the bulk electronic states with Λ_1 and Λ_3 symmetry, respectively. They assigned the S_t peak to the surface electronic states formed on the Ni(111) surface. By comparing the EDC of Ni(7 9 11) with that of Ni(111), we can consider that the B_1 and S_t peaks of the former correspond to the B_1' and S_t' peaks of the latter.

Figure 3 shows the photon energy dependence of the EDC observed on a clean Ni(7 9 11) surface. The peak positions of S_t and S_s are almost independent of photon

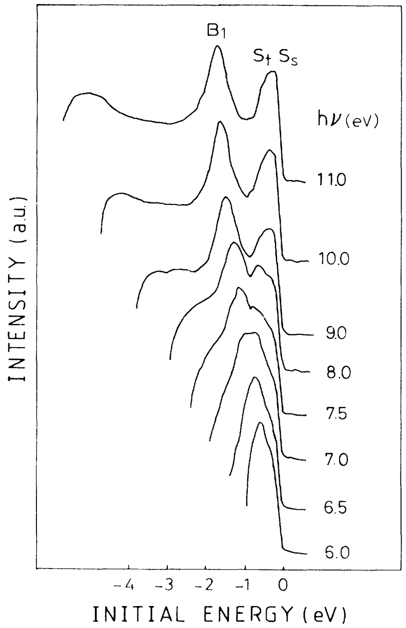

FIG. 3. Photon energy dependence of the EDC of a clean Ni(7 9 11) surface for p polarization ($\theta_i = 85.8°$, $\theta_e = 0°$).

energy as expected for a surface electronic state or a localized electronic state, whereas the B_1 peak is markedly shifted on varying photon energy. We have also examined the dispersion of the electronic states responsible for each peak and found that the electronic states responsible for the S_t and S_s peaks exhibited flat dispersions [9]. These behaviors are in good agreement with those reported for the B_1' and S_t' peaks of a clean Ni(111) surface [10,11]. Therefore we can safely conclude that the B_1 and S_t peaks of Ni(7911) correspond to the B_1' and S_t' peaks of Ni(111). Consequently, the B_1 peak can be assigned to a bulk electronic state while the S_t peak can be assigned to the surface electronic state associated with the Ni(111)-like terrace plane. But the S_t/B_1 intensity ratio of Ni(7911) is considerably lower than the S_t'/B_1' intensity ratio of Ni(111). The reduction of the intensity ratio probably arises from the situation where only a few atomic rows among the five rows in each terrace are contributing to the formation of the surface electronic state responsible for the S_t peak of Ni(7911) surfaces.

A peak corresponding to B_2' of Ni(111) should also appear in the case of Ni(7911) because it is associated with a bulk electronic state. Although the EDC of Ni(7911) exhibits the shoulder S_s at the position corresponding to the shoulder B_2' of Ni(111), the S_s peak has to be considered to be mainly associated with a surface electronic state, not with a bulk electronic state, since its intensity is markedly affected by alkali metal adsorption. However, we found that its intensity decreased only in the initial stage of Na adsorption up to 0.4 ML and thereafter stayed nearly constant, while the intensity of the S_t peak was still decreasing on further increasing Na coverage. This fact suggested that the S_s peak is, in reality, composed of two components where one is adsorption sensitive and the other is adsorption insensitive.

Figure 4 shows the EDC's obtained for p and s polarizations on a Li-adsorbed Ni(7911) surface (with Li/Ni Auger ratio $R=0.86$), together with the corresponding EDC's of the clean Ni(7911) surface. In the case of p polarization [Fig. 4(a)], the EDC of the Li-adsorbed state is very similar to that of the Na-adsorbed state, showing a marked intensity reduction in the S_t and S_s peaks. On the other hand, in the case of s polarization [Fig. 4(b)], the EDC is little affected by Li adsorption, indicating that all the photoelectron peaks observed there are associated with bulk electronic states. Therefore, we can assign the first band observed for s polarization in the region of -1–0 eV from the Fermi level to the bulk electronic state corresponding to B_2' of Ni(111), while the S_t and S_s peaks observed for p polarization are mainly due to surface electronic states. The above polarization dependence of EDC is in good agreement with the observation made by Himpsel and co-workers on Ni(111) [10,11], where it was shown that the B_2' peak associated with a bulk electronic state of Λ_3 symmetry strongly appeared for s polarization while the S_t' peak due to a surface electronic state strongly appeared for p polarization.

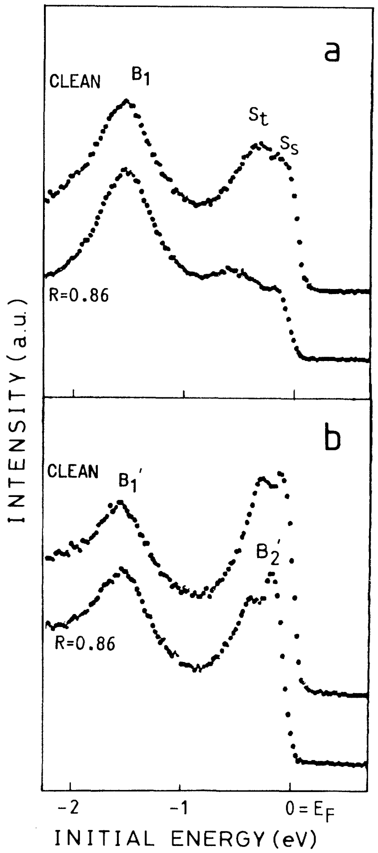

FIG. 4. EDC's measured on a clean Ni(7911) surface and its Li-adsorbed state (with Li/Ni Auger ratio, $R=0.86$) by the stimulating photon energy of 10 eV for (a) p polarization ($\theta_i=85.8°$, $\theta_e=0°$) and (b) s polarization ($\theta_i=28.8°$, $\theta_e=0°$).

The shape of the first photoelectron band (the B_2 peak) in the EDC of Ni(7911) obtained for s polarization is similar to the reported spectral shape of the B_2' band of Ni(111), which was well explained from the bulk band structures with the consideration of the spin population. All these facts indicate that the B_2 peak in the EDC of Ni(7911) for s polarization is dominantly due to the bulk electronic state, while the S_t peak observed in the p-polarization data of Ni(7911) is due to the surface electronic state corresponding to the one responsible for the S_t' peaks of Ni(111). As we have already mentioned, the S_s peak of Ni(7911) is composed of an adsorption-sensitive component and an adsorption-insensitive component. Seemingly, there is a small contribution of the B_2 peak in the region overlapping the S_s peak to give its adsorption-insensitive component. Since no photoelectron peak corresponding to the adsorption-sensitive S_s peak can be found in the case of Ni(111), we can conclude that it is characteristic of a Ni(7911) surface and most likely to be associated with the surface electronic state characteristic of the step. Possibly, the new boundary condition at step edges induces a splitting of the surface electronic state corresponding to that of Ni(111) into the two surface electronic states, one which is associated mainly with the terrace and the other being a new surface electronic state mainly associated with the step edge. We think that the former gives the S_t and the latter gives the S_s peak. Possibly, the latter surface electronic state is electronically screened at the middle of the terrace plane as has been suggested theoretically [12]. The terrace on Ni(7911) has five atomic rows, among which the atomic row at each terrace edge would be involved in the formation of the electronic state associated with the step edge. This implies that only two or three atomic rows on the central part of each terrace can effectively contribute to the formation of the surface electronic states responsible for the S_t peak. This seems to explain the reduction of the S_t/B_1 intensity ratio in comparison with the corresponding intensity ratio, S_t'/B_1', of Ni(111).

In conclusion, we believe that we were able to obtain in the present ARUPS study an evidence indicating the presence of a surface electronic state characteristic of the step edge as well as the formation of a surface electronic state associated with the Ni(111)-like atomic rows in the terrace plane.

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