Surface electronic structures of ferromagnetic Ni(111) studied by STM and angle-resolved photoemission

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Spin-polarized surface electronic states in Ni(111) have been examined using scanning tunneling microscopy (STM) and spectroscopy (STS) combined with high-resolution angle-resolved photoemission spectroscopy (HR-ARPES). Standing waves derived from the majority-spin Shockley surface state (SS) have been observed in the STM and dI/dV images. The fast Fourier transform (FFT)-dI/dV image at a different sample bias exhibited a circular contour in the reciprocal space. The radius of the FFT-dI/dV image was in agreement with that of the corresponding constant-energy contour given by the HR-ARPES. The majority-spin Shockley SS is partially occupied and disperses upward, crossing the Fermi level (E_F) at a wave number of $k_F = 0.081 \pm 0.005$ Å^{-1}. The effective mass (m^*) with respect to the free-electron mass (m_e) of the majority-spin Shockley SS was evaluated to be $m^*/m_e = 0.19 \pm 0.03$. The STS spectrum indicated a pair of the Shockley SS below and above E_F with an exchange splitting of ~190 meV. By the line-shape analyses of the HR-ARPES spectrum, the lifetime broadening at the $\bar{\Gamma}$ point was calculated to be 53.6 meV, which agrees well with the width (49 meV) of the steplike structure in the STS spectrum. The results from the STM/STS and HR-ARPES experiments were found to be mutually consistent.

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I. INTRODUCTION

Surface and interface electronic states exhibit much different structural and electronic properties compared to those in the bulk due to their low-dimensional nature. Knowledge of the surface and interface electronic states is indispensable in developing functional materials with advanced efficiency. Furthermore, by utilizing the spin degree of freedom, one can extend the possibilities of functional materials. Understanding the spin-polarized free-electron system is a key issue in the study of magnetic tunneling junctions as well as in the spin-field effect transistor.[1,2]

It is well known that the free-electron-like surface state, the Shockley surface state (SS), is present in the (111) surface of noble metals such as Cu, Ag, and Au.[3] This surface state has been extensively studied by the angle-resolved photoemission spectroscopy (ARPES) (Ref. 3) and scanning tunneling microscopy (STM).[4,5] It has also been reported that the Shockley SS exists in Ni, Pd, and Pt surfaces.[6,7] In particular, a ferromagnetic Ni has attracted considerable attention since a spin-polarized two-dimensional electron gas can be expected in the surface of this material. Recently, graphene (monolayer graphite) grown on Ni(111) surface has attracted much interest.[8,9] Highly spin-polarized surface states of Ni should play an important role in the injection of spin into the graphene. One can expect a ballistic spin transport along the graphene layer because of the prolonged spin-relaxation time due to its small spin-orbit coupling.[2] It is important, therefore, to quantitatively characterize spin-polarized surface states in Ni.

The Ni(111) surface state has long been studied and discussed.[10–18] The exchange-split Shockley surface states were first predicted by a one-step model photoemission calculation.[11] More recent theoretical works have also predicted two SSs, which are separated by 180–350 meV.[14–17] Early ARPES measurements of Ni(111) using lasers revealed two parabolic surface states with upward and downward dispersions at the $\bar{\Gamma}$ point of the surface Brillouin zone (SBZ).[13] The spin-split Shockley SSs above E_F were studied by the spin-resolved inverse photoemission spectroscopy (IPES).[12] The exchange splitting was estimated to be 106 ± 22 meV at room temperature at a position slightly removed from the $\bar{\Gamma}$ point.[12] Recently, we have done high-resolution angle-resolved photoemission spectroscopy (HR-ARPES) measurements at 10 K using synchrotron radiation.[18] Our HR-ARPES measurement has confirmed the existence of the majority-spin Shockley SS below E_F. However, taken at low temperature, the energy for the bottom of the parabolic band (−135 meV) is slightly lower than the value determined previously (−110 meV) at 140–155 K.[13] The result indicates that the energy shift toward the lower binding energy on heating also occurs in Ni(111) as observed for the Shockley SSs in noble metals.[19]

The Shockley SS in an artificial nanoisland of Ni(111) has been investigated by STM.[20] One would expect a steplike spectral feature at the bottom of the energy-band dispersion for the Shockley SS in this material, similar to that observed in the surfaces of noble metals.[4,5] However, such a steplike feature was absent in the previous scanning tunneling spectroscopy (STS) observations.[20] A more recent STM/STS study on Ni(111) has claimed that both majority- and minority-spin surface states exist below E_F, and the exchange splitting was evaluated to be ~60 meV.[21] The result does not agree with our HR-ARPES experiments at low temperature.[18] There exist serious contradictions between the STS/STM and ARPES measurements.

In order to resolve these discrepancies, we have carefully investigated the Shockley SSs in Ni(111) by means of both STM/STS and HR-ARPES at low temperature. The STM and STS with high spatial and energy resolution can probe both the occupied and unoccupied local density of states, which is not possible with ARPES measurements at low temperature alone. Furthermore, by the observation of the nanometer-scale standing wave (SW) caused by the step edges or point defects, one can evaluate the k dependence of the electronic states.[22] On the other hand, HR-ARPES with high momentum and energy resolution is a powerful tool for the direct observation of quasiparticles in the occupied states. One can determine coupling parameters of the electron-phonon and electron-electron interactions as well as the mean free path of conduction electrons, which are responsible for the electron-spin transport in nanospintronic devices. In the present study, we report that these complementary techniques actually give mutually consistent results for the Shockley SS in Ni(111) at low temperature.

II. EXPERIMENTAL CONDITIONS

The surface of single crystalline Ni(111) was prepared by repeated cycles of Ar^+ ion sputtering with an ion energy of 600 eV, subsequent annealing at 700 K in oxygen atmosphere of 4.0×10^{-10} mbar for several minutes, and annealing at 800 K without oxygen for half an hour. The STM and STS experiments were conducted at 4 K under ultrahigh vacuum, with a base pressure of 1.0×10^{-10} mbar or less, using a low-temperature scanning tunneling microscope (LT-STM, Omicron NanoTechnology GmbH). The STM images were acquired in the constant-current mode with a bias voltage V_s applied to the sample. The dI/dV images with closed feedback were acquired simultaneously with recording the STM images using a lock-in technique. The resulting STS data were averaged over 13 spectra to improve statistics.

The HR-ARPES experiments were performed with a spectrometer equipped with hemispherical electron analyzer (R4000, VG-SCIENTA) installed on the helical undulator beamline (BL-9) of a compact electron-storage ring at the Hiroshima Synchrotron Radiation Center (HiSOR).[23] Circularly polarized undulator radiation was used as the source of excitation photons. An incident photon energy of $h\nu$ =6.9 eV was chosen since the bulk-derived bands are located farthest from the surface state. It is also noted that the photoinonization cross-section ratio of the SS with respect to the bulk-derived state increases for photon energies below ~10 eV.[10]

We set the total-energy resolution at ΔE to be 4–6 meV and the angular resolution at $\Delta\theta$ equal to 0.2°–0.3° (momentum resolution Δk=0.003–0.004 Å^{-1}). The sample was mounted on a liquid-helium-cooled five-axis goniometer (i-GONIO LT, R-DEC Co.). The surface cleanliness was checked by an Auger electron spectroscopy. The low-energy electron-diffraction measurement indicated clear 1×1 spots.

III. RESULTS AND DISCUSSION

A. STM image and *dI/dV* map

Figures 1(a) and 1(b) show the STM image and the dI/dV map of Ni(111) surface at the sample bias voltage (V_s) of

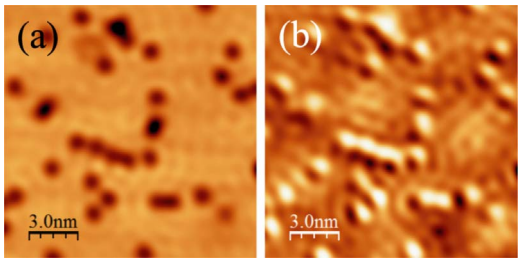

FIG. 1. (Color online) (a) STM image and (b) dI/dV map of the Ni(111) surface measured at 4 K (V_s=−50 mV, I=0.4 nA). These images were acquired at the same time.

−50 mV. These images were obtained for the same surface without changing any experimental parameters. Both images clearly show a SW that is spread isotropically around point defects.

In order to get more detailed information of the SW, fast Fourier transformation (FFT) was applied to the dI/dV image, and the image in the reciprocal space was obtained computationally. Figure 2 shows the thus-obtained reciprocal images, where the brighter portion indicates the more intense Fourier components. The FFT image shows a circular-shaped energy contour, which is similar to the well-known reciprocal images of Cu (111) and Au (111) near zero bias.[24] However, due to the thermal drift during the measurement, the circles were modified for several bias voltages. In order to extract the radii of the circles as a function of V_s, the several sizes measured for different directions have been averaged. The estimated radius became smaller as V_s decreased. For

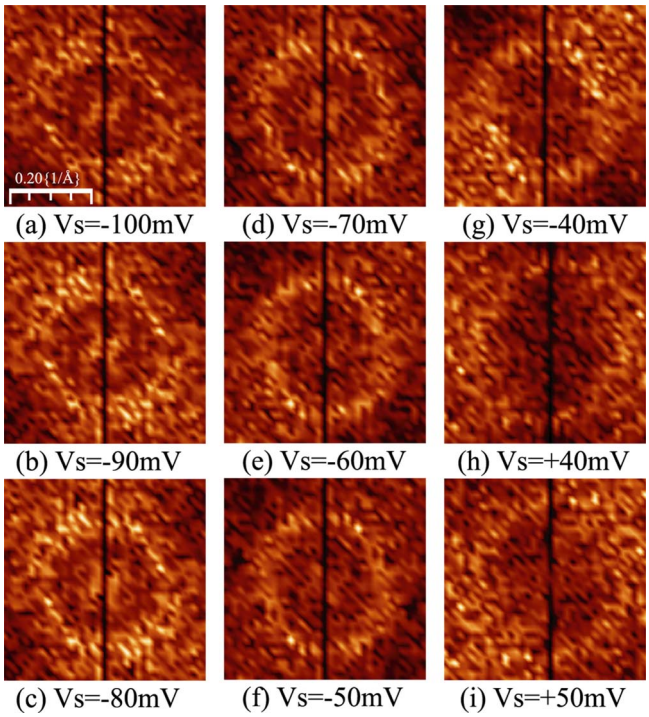

FIG. 2. (Color online) [(a)–(i)] Circular patterns obtained by the fast Fourier transformation of dI/dV images at sample bias voltages from (a) −100 mV to (i) +50 mV. The brighter dots represent the larger Fourier components.

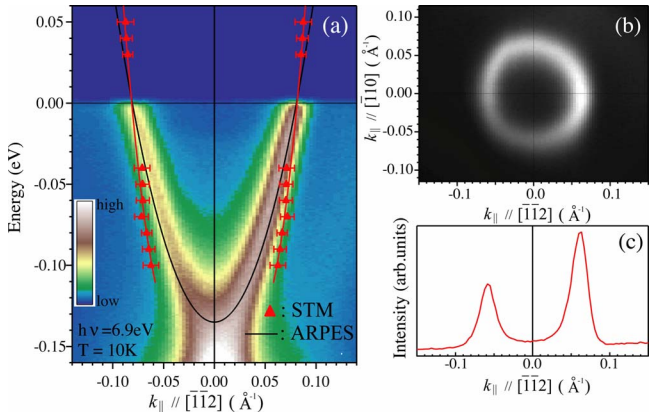

FIG. 3. (Color online) (a) The E-k relation obtained by the STM experiment is denoted by up triangles. Energy dispersion curve vs k derived by HR-ARPES is shown by the solid line. (Ref. 18). (b) The constant-energy surface of the Shockley SS at −50 meV. (c) The MDC of (b).

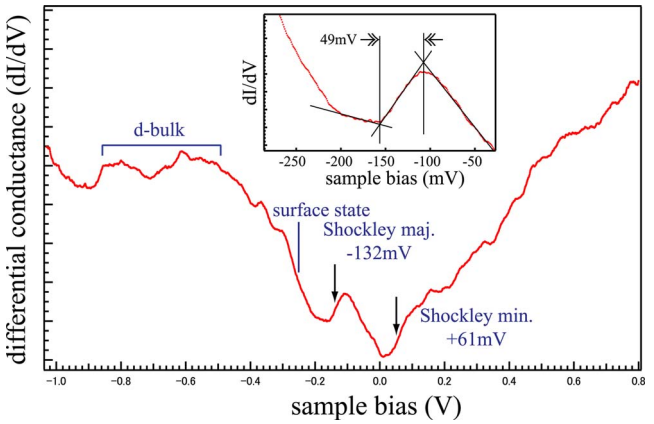

FIG. 4. (Color online) Experimental STS spectrum of the Ni(111) surface. This inset expresses the spectrum expanded at about −132 mV.

example, we found circular patterns with a radius of 0.14 Å^{-1} at −50 mV and 0.18 Å^{-1} at +50 mV, respectively. This indicates an upward energy dispersion of relevant electronic states. Such a reciprocal image has not been obtained below roughly −130 mV. For free-electron surface states, it is well known that the radius of the wave number in the FFT image acquired by the STM is twice as large as that obtained by ARPES.[4,25] For this reason, we can determine that the wave number of this electronic state at −50 mV is 0.07 ± 0.01 Å^{-1}.

Next we explore the correspondence between the STS/STM and HR-ARPES results. Figure 3(a) shows the observed energy-dispersion curve of the Shockley SS along the $\bar{\Gamma}\bar{M}$ direction. We have found that the bottom of the parabolic energy dispersion is located at -135 ± 5 meV at temperature of 10 K. We have also evaluated the effective mass as $m^* = (0.19 \pm 0.03) m_e$ using the formula $m^* = \hbar^2 [d^2 \epsilon_k / dk^2]^{-1}$, where ϵ_k represents the energy of a band at k. The strong intensity at the bottom of the Shockley SS was derived from the surface state with a downward dispersion.[13] The Fermi wave number was evaluated by fitting the momentum-distribution curve (MDC) at E_F to a Lorentzian function as $k_F = 0.081 \pm 0.005$ Å^{-1}. Figure 3(b) represents the intensity plots of the constant-energy surface of the Shockley SS at −50 meV. Here the intensity was integrated over ±10 meV. We can find a circular constant-energy surface centered at the $\bar{\Gamma}$ point. Figure 3(c) shows the MDC of Fig. 3(b). One can clearly see two peaks separated by 0.06 Å^{-1}, which is in very good agreement with the radius of the above dI/dV map. One notices in Figs. 3(a)–3(c) that the photoemission intensity at negative wave numbers is weaker than that for $k_{\parallel} > 0$. We assume that this asymmetric intensity comes from the matrix-element effect which is dependent on the geometrical configuration of the ARPES measurements and light polarization.

The E-k relations extracted from the circular-shaped constant-energy contours of the Shockley SSs originally shown in Fig. 2 are depicted with the filled triangles in Fig. 3(a). Here it is found that the dispersion curve deduced from the STM experiment is consistent with the HR-ARPES result. However, the slope of the dispersion obtained by the STM looks slightly steeper than the photoemission result. The deviation comes from the presence of the modulated surface potential as discussed for the Au(111) surface.[22] Here we have corrected the energy-band dispersion obtained from the HR-ARPES result by taking into account the relationship $k = (k_F + k_{\parallel})$, where $k_{\parallel}$ is the wave number of the Bloch wave state as measured by the ARPES without the modulated potential. The corrected dispersion (the solid line in Fig. 3) shows an even better correspondence with the STM result. We thus conclude that the occupied electronic states contain only the majority-spin states, where the minority-spin Shockley SS is pushed completely above E_F by the exchange interaction.

B. STS spectrum

Next, we examine the STS spectrum, namely, dI/dV as a function of V_s, for the Ni(111) surface. It is well established that the local density of states (LDOS) is reflected in the STS spectrum. A derivative of tunneling current can be expressed as follows:[26]

$$\frac{dI}{dV} \propto e\rho_s(eV_s)T(eV_s, eV_s) + \int_0^{eV_s} \frac{d}{dV_s}[\rho_s(E)T(E, eV_s)]dE, \tag{1}$$

$$T(E, eV_s) = \exp\left\{\frac{-2d}{\hbar}\sqrt{2m\left(\frac{\phi_s + \phi_t}{2} - E + \frac{|eV_s|}{2}\right)}\right\}. \tag{2}$$

Here, ρ_s denotes the density of states of the sample at the vacuum boundary. $T(E, eV_s)$ gives the tunneling probability of an electron at energy E measured with respect to its individual E_F. d represents the tip-sample distance and ϕ_s and ϕ_t are the work functions of the sample and tip, respectively.

Figure 4 shows the STS spectrum obtained at the terrace without any defect within a width of 12 nm. Here one can

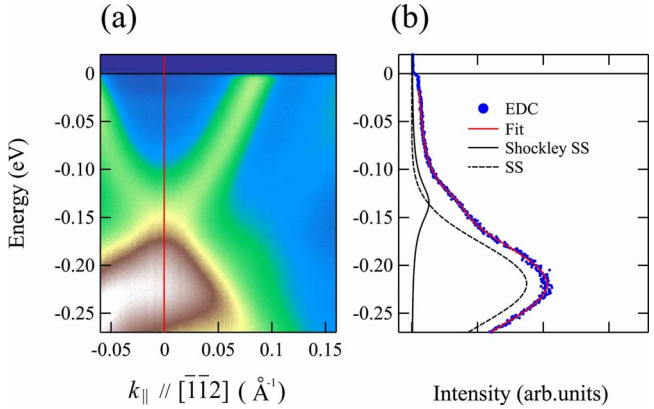

FIG. 5. (Color online) (a) The energy dispersion of the Shockley SS of Ni(111). (b) EDC at the $\bar{\Gamma}$ point.

observe several peaks and the steplike structures at $V_s = -132$ mV and +61 mV, where a clear dip can be found just below each steplike structure. In this spectrum, the feature near E_F is different from the earlier STM result.[20] The steplike structure near E_F in the STS spectrum of the noble-metal (111) surfaces has been reasonably explained by the Shockley SS as a two-dimensional free electron-gas system.[5] In the present experiment, we find two steplike structures near E_F, namely, at −132 meV and +61 meV. We attribute them to the exchange-split Shockley SSs above and below E_F. Below E_F, we have obtained the circular contours in the reciprocal space and also observed the energy dependence of this circle, corresponding to the lower-lying steplike structure in the STS spectrum. Therefore, the observed rising edge at −132 meV as denoted by the arrow comes from the bottom of the parabolic energy dispersion in the Shockley SS of Ni(111).

However, no corresponding circular-shaped FFT image has been observed for the second steplike structure located at higher energy (>+60 meV). The Shockley SS in the minority-spin channel just above E_F has been probed by the spin-resolved IPES.[12] We believe that this higher-energy structure originates from the Shockley SS in the minority-spin channel. Previous theoretical work has shown the overlap of the minority-spin Shockley SS with the projected bulk bands.[15] The absence of the circular-shaped Fourier components might be due to the fact that the minority-spin Shockley SS overlaps with the projected bulk band. Referring to the previous study of the (111) surface of a noble metal by STM,[5] we assigned the band edge of the majority-spin Shockley SS to be −132 meV and the edge of minority-spin Shockley SS to be +61 meV as indicated in Fig. 4.

The width of the steplike structures for the majority-spin state is 49 meV as shown in the inset of Fig. 4. The width should give the lifetime broadening of the quasiparticle at the bottom of the Shockley SS in Ni(111). In order to estimate lifetime broadening at the $\bar{\Gamma}$ point [the line in Fig. 5(a)], we have analyzed an energy distribution curve (EDC) obtained from HR-ARPES. Figure 5(b) shows the fitting result of the EDC at the $\bar{\Gamma}$ point. We have simulated the broad surface state with downward dispersion (SS) using a Gaussian distribution [the black dashed line in Fig. 5(b)] and fit the Shockley SS to a Lorentzian [the black solid line in Fig. 5(b)]. The lifetime broadening of the Shockley SS at the $\bar{\Gamma}$ point was evaluated to be 53.6 meV, which shows good agreement with the STS result.

In a previous work, we have demonstrated that the electron-phonon coupling in the Shockley SS is very weak.[18] Combined with the line-shape analyses, we conclude that the intrinsic lifetime broadening is dominated by the electron-electron interaction.

The width of MDC at E_F indicates $\delta k \sim 0.027$ Å^{-1}. The mean-free path of the quasiparticle is evaluated to be $l = \delta k^{-1} \sim 37$ Å, which is determined by the point defects as seen in the present STM images. Based on the observed energy-band dispersion, we have estimated the Fermi velocity as $v_F = 3.57 \times 10^5$ m/s. The relaxation time (or lifetime) of the quasiparticle is calculated to be $\tau = l/v_F = 1.04 \times 10^{-14}$ s.

Finally, we may remark on one of the possible reasons for the splitting of the Shockley states observed in the previous STM result.[21] Recently Ono *et al.* reported that the electrostatic potential becomes deeper near the step edges.[27] If one measures signals from the step edges as well as away from the step edges, one may detect peak splitting due to the potential difference. If this is true for the Ni case, the two energy-band dispersions observed in the previous STM study may have essentially the same origin, namely, the majority-spin Shockley state but are split due to the potential difference. In the present study, we have only observed the standing waves induced by the point defects on the flat area. We, therefore, did not observe splitting due to the potential difference.

IV. CONCLUSION

In this study, we have observed a standing wave relevant to the majority-spin Shockley SS of Ni(111) and obtained the circular constant-energy contour in reciprocal space at given energies. On the other hand, a circular pattern ascribed to the Shockley SS for the minority-spin state has not been obtained clearly probably due to the overlap with the projected bulk bands. From our STS spectrum, the exchange splitting of the Shockley SS is evaluated to be ~190 meV. Our HR-ARPES experiment has clearly shown that the majority-spin Shockley SS disperses upward with an effective mass of $m^* = (0.19 \pm 0.03) m_e$ and crosses E_F at $k_F = 0.081 \pm 0.005$ Å^{-1}. The results agree well with the E-k relation extracted from the dI/dV image. The lifetime broadening at the $\bar{\Gamma}$ point is estimated to be 53.6 meV from the EDC line width, which agrees well with the steplike feature width 49 meV in the STS spectrum. The present STS and HR-ARPES results clearly indicate that the majority-spin Shockley SS is partially occupied and crosses E_F, while the minority-spin state is completely pushed above E_F.

The present STM and photoemission measurements have been performed without spin resolution. To further confirm the present conclusion, spin-resolved measurements are highly desirable.

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