Photoemission study of the surface band structure of the reconstructed Mo(001) surface

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We have investigated surface-electronic-dispersion relations of a Mo(001) surface using angle-resolved photoemission spectroscopy. We present surface band structures of the reconstructed Mo(001) surface below the transition temperature (T_c). Electronic characteristics including energy dispersion relations, symmetries of the surface states, and resonances are determined and discussed in terms of their significance in reconstruction. The physical implications of the characteristic changes upon crossing T_c are further discussed in detail.

I. INTRODUCTION

Extensive experimental and theoretical studies concerning the spontaneous reconstructions of clean W(001) and Mo(001) surfaces have been made since their discoveries.[1,2] Despite the similarity in lattice structures as well as in electronic configurations, the W(001) and Mo(001) surfaces undergo distinctly different surface reconstructions from $p(1\times1)$ to a commensurate $c(2\times2)$ and an incommensurate $c(2.2\times2.2)$, respectively, when cooled below transition temperatures (T_c). One of the issues of previous works is to understand the nature of a strong surface state quite near the Fermi energy (E_F), the so-called "Swanson hump," observed on these surfaces at room temperature in order to ellucidate a driving mechanism for the transitions.[3–14]

For W(001), the basic electronic characters of the surface states and resonances have been relatively well documented to date.[3–11] However, the same may not be obviously true for Mo(001), where information about the electronic properties of surface states and nearby resonances, and their roles in reconstruction, are still lacking. In this paper, we present a full description of surface band structures and fundamental electronic characters of the surface states and resonances for Mo(001), especially at temperatures below T_c. Since we observed several characteristic changes of these properties upon crossing T_c in regard to energies, band connectivity, and Fermi wavevector ($\mathbf{k}_\parallel^F$) dimensions throughout the irreducible part of the surface Brillouin zone (SBZ), we focus our discussion on these differences emphasizing any correlations with reconstruction.

The structure of this paper is as follows. A description of the experimental settings is given in Sec. II, which is followed by the results of angle-resolved photoemission (ARP) measurements of a Mo(001) surface above and below T_c in Sec. III. We present experimental dispersion relations and symmetries of the surface states and resonances in this section. The results are discussed in comparison with previous studies and our theoretical surface band calculation reported elsewhere.[15] Physical implications of these characters are further discussed regarding reconstruction before a summary in Sec. IV.

II. EXPERIMENTAL PROCEDURES

The experiment was performed using synchrotron uv radiation on the Institute for Solid State Physics (ISSP) beamline BL-18A at the Photon Factory in Japan. The beamline collects 2 mrad horizontal divergence of synchrotron radiation and can be used for photon energies from 10 to 150 eV with a constant deviation angle grazing incidence monochromater. This beamline is also equipped with an ARP spectrometer (VG ADES 500), and allowed typical energy and angular resolutions less than 150 meV and 1° for the present work. The sample surface, oriented within $\pm0.2°$ to a (001) crystalline plane, was cleaned by a well-known recipe,[13] and produced a sharp (1×1) LEED pattern with fuzzy and weak intensity distributed near $\bar{M}=\pi/a(1,1)=1.4$ A^{-1} position in the SBZ at room temperature, and an incommensurate $c(2.2\times2.2)$ pattern at temperatures below $T_c=230$ K.[1,2]

A quartet of extra spots near $\bar{M}$ from the reconstructed surface stayed strong and sharp for at least 20 min, and was still discernible after 40 min under a base pressure of about 2×10^{-11} Torr. Interestingly, we were not able to observe the $(7\sqrt{2}\times\sqrt{2})$ LEED pattern for temperatures down to 52 K, in contradiction with recent studies.[16,17] In order to cool the sample, we used a cold head of 20 K at the tip, which was thermally connected to the sample through copper braids. The sample was heated by electron-beam bombardment to its rear surface, and the

surface temperature was monitored with a *W*26%Re-*W*5%Re thermocouple spot welded to the edge of the rear surface. The sample temperatures measured by the thermocouple matched with those obtained using an optical pyrometer to within ±5 K. Using a typical routine for measuring the work function by tracing the tail of secondary electrons with a suitable bias applied on the sample, we also obtained a work function of 4.4±0.2 eV.

A typical routine of data-taking procedure is as follows. After flashing the sample to 2500 K, chamber pressure quickly decreased to low 10^{-11} Torr, and the sample cooled down to near 60 K in about 3 min. We then observed a well-defined $c(2.2\times2.2)$ LEED pattern from the reconstructed surface, and collected five or six spectra for about 20 min before a next flashing. We often checked the LEED pattern after a cycle of data collection, which normally maintained a sharp $c(2.2\times2.2)$ LEED pattern signaling the reconstruction.

The ARP spectra in this work were obtained with the incoming photons, polarization vectors, and a detector in a particular mirror plane so that states of even symmetry with respect to the mirror plane can be primarily detected according to Hermanson's rule when spin-orbit coupling is ignored.[18] We have, however, observed states of odd symmetry which is also due to the nonideal experimental conditions such as imperfect polarization of synchrotron radiations, and inaccurate alignment of the sample with incoming photons. The symmetry of the $p(1\times1)$ LEED pattern at room temperature was used as a guide for alignment of the photons within a specific mirror plane whenever necessary. During the entire course of the experiment, extra care has been taken to avoid any contaminations of the surface, especially hydrogen adsorption.

III. RESULTS AND DISCUSSION

Figure 1 shows typical ARP normal emission spectra at the center of SBZ ($\mathbf{k}_\parallel=0$ A^{-1}; $\bar{\Gamma}$) for a clean (*A*), and a hydrogen contaminated (*B*) Mo(001) surface. The state S_1 of binding energy $E_b=-0.2$ eV below E_F disappears quickly with slight hydrogen contamination of about 0.1 L (1 L$=10^{-6}$ Torr s) exposure, showing strong surface sensitivity. This state also shows nondispersive character with incident photon energy as depicted in Fig. 2, and has been identified as a true surface state previously.[3,13] We thus reconfirm the surface nature of this state, which is further supported by our calculation.[15] In contrast, the state of $E_b=-1.2$ eV remains almost unaffected and is identified as a bulk state B_1, together with a state at $E_b=-4.2$ eV as B_2. The remarkable thing is that, as will be presented later in Fig. 3, S_1 becomes sharper and stronger at low temperature for the reconstructed surface, in contrast to the case of W(001) where it disappears.[5]

The states of $E_b=-0.6$ and -3.4 eV, although their surface sensitivity is obscured by degenerate hydrogen-induced states, are identified as surface resonances SR_1 and SR_3, respectively, following the calculations which show that more than half of their charges reside on a surface or selvege region.[15,19,20] The basic nature of a resonance state is also seen in strong nondispersiveness in Fig. 2, where momentum perpendicular to the surface varies with photon energy. The nondispersive characters of the surface state and resonances are demonstrated by the vertical dashed lines for S_1 and SR_3 in Fig. 2. As discussed later in this section, the resonance SR_1, although appearing weak with photons of energy 21.22 eV, does have a vital role in the reconstruction.

A series of representative ARP spectra are displayed in Fig. 3 with two-dimensional wave vectors $\mathbf{k}_\parallel$ along the $\bar{\Delta}$

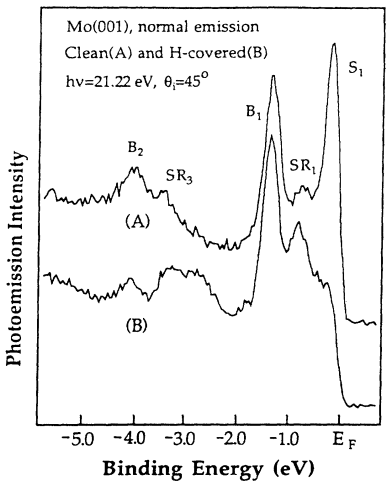

FIG. 1. Typical normal emission ARP spectra at $\bar{\Gamma}$ for a clean (*A*) and a hydrogen covered (*B*) Mo(001) surface at room temperature, demonstrating surface sensitivity of the surface state S_1 ($E_b=-0.3$ eV). Hydrogen-induced surface states are located in the vicinity of the surface resonances SR_1 and SR_2 of the clean surface. We note that the bulk states B_1 and B_2 remain almost unaffected.

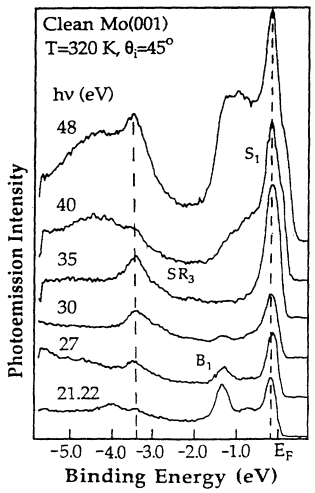

FIG. 2. Normal emission ARP spectra at $\bar{\Gamma}$ for a clean Mo(001) surface with varying incident photon energy. The nondispersive character of the surface state and resonances (especially for SR_2) is evident as marked with dashed lines.

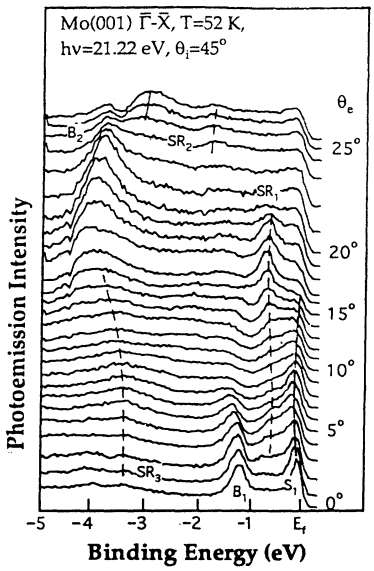

FIG. 3. A series of ARP spectra of the reconstructed Mo(001) surface along the $\bar{\Delta}$ axis $\bar{\Gamma}$-$\bar{X}$ or (10) direction at 52 K. Dispersions of the surface state S_1' and surface resonances SR_1' and SR_2' are represented by the solid and dashed curves, respectively. Notice that the surface state and resonances near E_F are well resolved and stay nearly flat with wave vector $\mathbf{k}_\parallel$.

azimuth ($\bar{\Gamma}$-$\bar{X}$) or (10) direction for a reconstructed Mo(001) surface at 52 K. Here, dispersions of the surface state S_1' and resonances SR_1', SR_2', and SR_3' are marked with solid and dashed curves, respectively. A normal emission spectrum of $\mathbf{k}_\parallel=0$ A^{-1}($\bar{\Gamma}$) is located in the bottom, while the top spectrum has $\mathbf{k}_\parallel=0.95$ A^{-1}, close to the zone boundary $\bar{X}$. Similar spectra along the $\bar{\Sigma}$ azimuth have already been presented in a previous paper.[12]

The spectra were obtained with photons of energy 21.22 eV, incident 45° off from the surface normal. Since polarization vectors of the incident light were in the (100) mirror plane, states of even symmetry are detected in this alignment as mentioned earlier. One can notice that S_1 moves back and forth slightly toward E_F with $\mathbf{k}_\parallel$, but stays almost flat within ± 0.20 eV before it disappears at $\mathbf{k}_\parallel=0.59$ A^{-1}. This rather long extension of S_1' has been controversial in previous experiments,[13,14] or in calculations where the reconstruction has not been considered.[15,19,20] Similar behaviors of the surface states were also observed along the $\bar{\Sigma}$ axis ($\bar{\Gamma}$-$\bar{M}$) or (11) direction.[12]

The surface resonance SR_1' is well resolved from the surface state S_1' as apparent in the spectra up to $\mathbf{k}_\parallel=0.78$ A^{-1}, where SR_1' nearly disappears. The existence of this resonance is well separated from S_1' and has not been clearly recognized previously. Smith and Kevan[13,14] showed their corresponding ARP spectra at room temperature, where separation of these peaks are not as obvious as in our spectra from the low-temperature phase. Since our room-temperature spectra also show strong S_1' at least up to $\mathbf{k}_\parallel=0.44$ A^{-1}, which can easily be quenched by a small amount of hydrogen contamination, the state cannot be a degenerate hydrogen state as discussed in detail later in this section.

We notice that S_1' and SR_1' increase their spectral intensity significantly upon cooling the sample below T_c. This effect was also found for S_1 and SR_1 along $\bar{\Sigma}$ (see Fig. 4 in Ref. 12). The enhanced features of these states at low temperature reflect their contributions in reducing the total free energy through reconstruction. We interpret this phenomena as being indicative of the fact that the reconstruction may not be confined to the outermost surface but can extend to the second or lower layers to some extent. This hypothesis is further supported by theoretical works suggesting that not only the in-plane $\bar{M}_5$ phonon but also the out-of-plane $\bar{M}_1$ phonon be involved in the reconstruction.[4,21,22] A surface-sensitive X-ray-scattering experiment may be useful to clarify this point as was done for a W(001) surface.[23] Another surface resonance SR_3' is seen at $E_b=-3.4$ eV at $\bar{\Gamma}$, and remains nearly dispersionless up to $\mathbf{k}_\parallel=0.44$ A^{-1} along $\bar{\Delta}$. We do not observe any significant differences for the behavior of SR_3' in spectra between room- and low-temperature phases.

The behaviors of the surface state and resonances described above appear in a graphic representation of the surface band structures in Fig. 4 for $\mathbf{k}_\parallel$ along $\bar{\Sigma}(a)$ and $\bar{\Delta}(b)$. Symmetries of the state have been assigned in comparison with our calculations reported elsewhere,[15] and were confirmed experimentally for some of the states as discussed below. These symmetry assignments generally agree with those found in the projected bulk band structure (PBBS) in previous calculations.[19,20] We also found that the overall features of the dispersion relation for the surface at room temperature agree with previous measurements.[13,14]

As mentioned earlier, the surface states S_1 and S_1' along $\bar{\Sigma}$ and $\bar{\Delta}$ stay nearly nondispersive, extending far out toward the zone boundaries. In fact, these states are found to cross E_F at $\mathbf{k}_\parallel=0.65$ A^{-1}, and 0.59 A^{-1} along the $\bar{\Sigma}$ and $\bar{\Delta}$ directions, respectively, and such crossings for the whole $\frac{1}{8}$ irreducible SBZ constitute a two-dimensional Fermi-surface contour. We have reported that the Fermi-surface contour has parallel segments perpendicular to the $\bar{\Sigma}$ direction, which enhances a Peierls-like $2k_F$ instability to drive the reconstruction.[12] Note that the E_F crossing along $\bar{\Sigma}$ accounts for the wave vector of the reconstruction $q_\parallel=2\mathbf{k}_\parallel^F=1.30$ A^{-1}, in close agreement with low-energy electron diffraction (LEED),[1,2] and the Kohn anomaly along this azimuth.[21,22]

As seen in Fig. 4(a), we notice that the dispersion relations between room- and low-temperature surfaces are quite similar if we ignore the enhanced spectral intensities of the states near E_F at low temperature. Within experimental error, we do not directly observe any clear gap openings at zone boundaries near E_F, which might be smaller than the energy resolution of 140 meV. One may interpret this similarity of band structures in terms of the degree of reconstruction at room temperature. Previous LEED studies argued that the room-temperature phase is

an unreconstructed ordered $p(1\times1)$ rather than a disordered $c(2.2\times2.2)$ phase.[2] If that is the case, then it would be surprising not to observe any perceptible gap openings considering relatively large elastic energy involved in the reconstruction which has to be compensated by electronic energy through strong coupling between nonadiabatic electrons near E_F and phonons.

Similar arguments have been applied to reconstruction of the W(001) surface, where a significant gap opening of about 0.5 eV at $\overline{M}$ due to $\overline{M}_5$-type distortion was predicted.[24] Such a sizable splitting, however, has not yet been found experimentally. On the other hand, previous synchrotron x-ray-diffraction studies showed that the structure of the $p(1\times1)$ phase is actually a disordered $c(2\times2)$ phase, losing long-range order due to the randomly placed domain walls which destroy the coherence of the reconstruction.[23] Therefore we propose that the phase above T_c for the Mo(001) surface may be more likely a disordered $c(2.2\times2.2)$ rather than an ordered $p(1\times1)$ phase. This point can also be confirmed experimentally as was done for W(001).[23]

We now look into the details of the dispersion relations shown in Fig. 4 by referring to PBBS in previous studies.[19,20] The most intriguing aspect in Fig. 4 is that the true surface states, S_1 and S_1', exist not only in the symmetry gaps but also in the allowed region near the zone center. This feature was also found for W(001), and has been a challenging subject of intensive theoretical studies, but has been left unresolved completely yet.[6–11,19,20] One finds that S_1 resides briefly in the odd symmetry gap, and in the absolute gap before it crosses E_F along $\overline{\Sigma}$. However, S_1' lies in the vicinity of an even symmetry gap along the $\overline{\Delta}$ azimuth.

In order to cross-examine theoretical predictions for the symmetries of the states, we attempted to determine these experimentally by polarization dependence of spectral intensity. Figure 5 shows spectral changes when an incidence angle θ_i of the photon varies for the reconstructed surface. In Fig. 5(a), we observe that the relative intensity of S_1 with respect to B_1 increases with incidence angle remarkably, demonstrating the dominant even symmetry of $d_{3z^2-r^2}$ orbital character for S_1 at $\overline{\Gamma}$, in agreement with recent theories.[15,19,20] The ratio becomes almost doubled at $\theta_i=65°$, as compared to the one at $\theta_i=35°$, while it is normally found to be about 1.3 at $\theta_i=45°$. Such a trend was also observed at other regions in SBZ with reduced values of the ratio as other orbital characters increase with $\mathbf{k}_\parallel$.

We thus find that the surface states are mainly of even symmetry along both $\overline{\Sigma}$ and $\overline{\Delta}$ azimuths. As mentioned

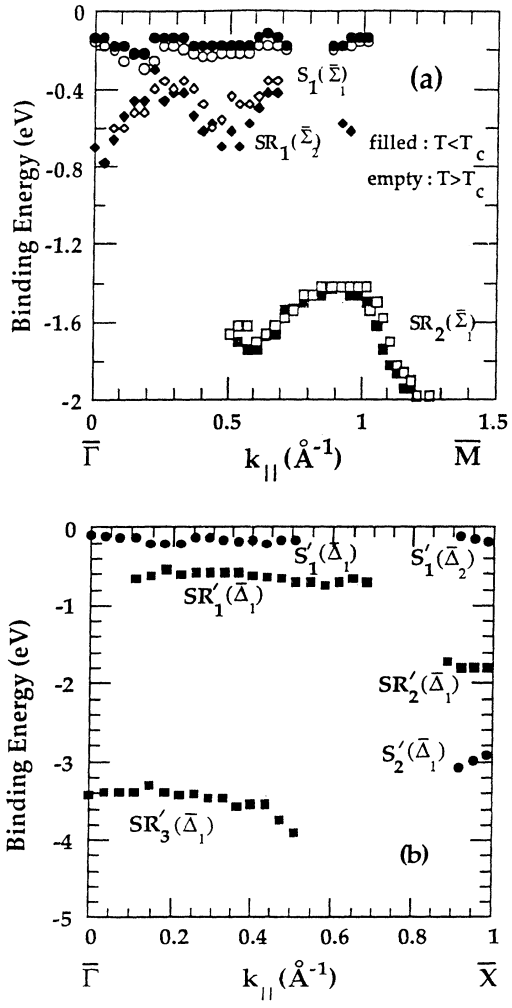

FIG. 4. Experimentally determined surface dispersion relations of the reconstructed Mo(001) surface at 52 K along $\overline{\Sigma}(\overline{\Gamma}$-$\overline{M})$ (a) and $\overline{\Delta}(\overline{\Gamma}$-$\overline{X})$ (b) directions. Notice the similarity of the band structures for above and below T_c, which is indicative of no clear gap opening at the zone boundary $\overline{M}$ within experimental error. We also observe the well-resolved surface states S_1, S_1' and resonances SR_1, SR_1' to the extended range in SBZ.

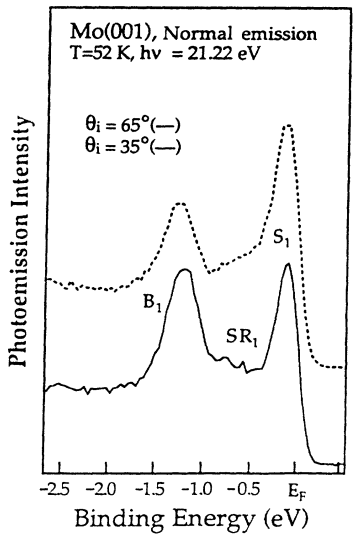

FIG. 5. Normal emission spectra of the reconstructed Mo(001) surface with varying photon incidence angle θ_i, showing polarization dependence of S_1, and SR_1 states. It is clearly shown that S_1 is primarily of even symmetry.

earlier, we note that imperfect polarization of synchrotron radiation allows a nonvanishing intensity even with photons at a normal incidence $\theta_i = 0°$. We also notice a weak surface state seemingly of mixed symmetry near the zone boundary along $\bar{\Delta}$ in Fig. 4(b). As reported earlier,[12,15] it stems from several degenerate bulk bands at the zone boundary. It is interesting to note that the symmetry of SR_1 is primarily odd along $\bar{\Sigma}$, while that of SR_1' is even along $\bar{\Delta}$ as suggested in the calculations.[15]

We should mention that S_1' extending about 0.59 A^{-1} along $\bar{\Delta}$ has not been detected previously in room-temperature measurements with a photon energy of 20 eV, but instead, a hydrogen-induced state having dispersion quite similar to S_1' in this work was observed with a photon energy of 40 eV.[13] As described briefly earlier, during the entire course of the present experiment, we have repeatedly and carefully checked the possibility of hydrogen contamination. We estimate maximum possible hydrogen exposure of about 0.03 L during a cycle of data collection. Even if we consider the effect of enhanced sticking probability at low temperature, the amount of exposure should not be enough to cause a hydrogen state to appear.

In fact, a mild flashing to 700 K over the desorption temperature of the hydrogen atom did not change the spectral features in any details. We thus believe that S_1' is a state from the clean reconstructed surface. Similar controversy with previous work is found for a state of binding energy at about -1.8 eV near the zone boundary, and we assign a surface resonance SR_2' for this feature due to its somewhat insensitivity to hydrogen contamination, and the presence of a symmetry (odd) gap in PBBS. by the same token, we identify surface resonances SR_2, SR_3 (not shown), and SR_3' for the states along $\bar{\Sigma}$ in Fig. 4(a), and along $\bar{\Delta}$ in Fig. 4(b), respectively. These surface resonances are well reproduced in most of the previous calculations, except SR_2'.

IV. SUMMARY

In summary, we measured the dispersion relations of the surface states and resonances of a reconstructed Mo(001) surface showing a $c(2.2\times2.2)$ LEED pattern. We have also identified symmetry of the states. Most of the experimental results agree qualitatively well with recent experimental and theoretical studies but differ in several important features, which are believed to be strongly related to reconstruction. One of these is that the surface states near E_F, primarily of even symmetries along $\bar{\Sigma}$ and $\bar{\Delta}$ azimuths, are well resolved with nearby the surface resonances in both directions.

The enhanced and better resolved surface states and resonances at low temperature might indicate that the reconstruction may smear into the subsurface layers. Furthermore the close similarity of the surface band structures above and below T_c implies that the room-temperature phase may be a disordered $c(2.2\times2.2)$ than an ordered (1×1) phase. These hypothetical conclusions, however, have yet to be confirmed by a direct-probing experiment, such as surface-sensitive x-ray diffraction, as was done for W(001).

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