Surface band structure of Al(1 0 0) studied with high-resolution angle-resolved photoelectron spectroscopy

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From an examination of the Al(1 0 0) surface band structure with high-resolution angle-resolved photoelectron spectra, we identified three surface states. Features in the surface band structure predicted theoretically were confirmed experimentally, including the dispersion of the surface state within the narrow band gap centered at ¯X, an avoided crossing between two surface states along ¯ΓX, and the dispersion of the surface state within the symmetry gap along ¯ΓM. The electron–phonon coupling strength of the surface state at ¯Γ was determined. Our results indicate that there is no thermally induced defect on Al(1 0 0) from 90 to 420 K. Our photoemission data serve as reference for future investigation and motivate re-examination of many systems with contemporary photoemission instruments.

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1. Introduction

The surface of a single crystal of aluminium, a trivalent nearly free-electron-like metal, has long been considered a model system to test the validity of diverse theoretical and experimental approaches. Among many surface properties, the surface states of aluminium have attracted much interest since they were reported experimentally in 1978 [1,2]. The results from these early measurements of angle-resolved photoemission showed that the surface states of aluminium exist both inside and outside the projected bulk band gaps. Numerous theoretical investigations explored this behavior; an extensive list is found in Ref. [3]. Surface states are generally agreed to exist in not only the absolute band gap but also “the symmetry gap” [4,5] (also called “filled band gap” [2] and the “partial Bragg reflection bulk energy gap” [6] by various authors). The complete surface band structures of aluminium were reported in the studies based on the geometry of a semi-infinite crystal [3,4].

In contrast to the theoretical results, the experimental data for aluminium surface band structures are far from complete. In the case of Al(1 0 0) (cf. Fig. 6 in Ref. [3] and Fig. 8 in Ref. [4] for the results of calculations), several authors reported the dispersion of the surface state near ¯Γ [1,2,7,8]; the surface state near ¯X was observed, but only its binding energy was reported [7]. Many features of the surface band structure predicted theoretically have not been observed, such as the dispersion of the surface state within the narrow band gap near ¯X, the surface resonance and the avoided crossing between the two surface states along ¯ΓX, and the surface state within the symmetry gap along ¯ΓM. This scarcity of experimental data resulted partly from the difficulty of measuring angle-resolved photoemission in an off-normal geometry with traditional electron energy analyzers. In recent photoemission experiments, electron energy analyzers were equipped with a two-dimensional channel plate, but predicted features in the surface band structure of Al(1 0 0) were still not observed [9,10]. A common practice to evaluate a theoretical approach involves a comparison of its results with experimental data. The failure to observe many theoretically predicted features in experiments casts doubt on the validity of the theoretical works on the Al(1 0 0) surface.

To address this discrepancy, we re-examined the Al(100) surface with high-resolution angle-resolved photoelectron spectroscopy (ARPES). With the improved angular resolution and sampling accuracy, we measured the photoemission along the high-symmetry lines in the surface Brillouin zone of Al(100), and identified several theoretically predicted features in the surface band structure. Our results not only confirm the predictions from
preceding theoretical works but also provide experimental data of high quality as reference for future investigations.

2. Experiment

The experiments were performed at an end station attached to the ultra-high-resolution and high-flux U9 cylindrical-grating beamline (BL21B) at National Synchrotron Radiation Center, Taiwan. An Al(1 0 0) single crystal (diameter 1 cm, miscut <0.1°) was mounted on a manipulator. The sample temperature, variable from 60 K to 1000 K, was measured with a thermocouple junction (type E) mounted beside the sample. The Al(1 0 0) surface was cleaned with 1.5-kV Ar-ion sputtering and annealing at 450 °C in repeated cycles until a sharp p(1 X 1) low-energy electron diffraction (LEED) pattern was obtained. Photoemission was measured with the photon energy varied from 21 to 54 eV. The distribution of photoelectron energy was recorded with an electron energy analyzer (Sciencta SES200) equipped with a two-dimensional channel plate and a charge-coupled-device camera, allowing 96 spectra at various emission angles to be collected concurrently with angular resolution 0.125°. The axis of the acceptance cone of the analyzer (A axis) and the incident axis of the photon beam (P axis) were fixed at angle 45° to each other. The polarization of the incident photons and the angular dispersion plane of the analyzer both lay in the plane spanned by the A and P axes. To acquire the photoemission spectra over a wide range of k∥ (the component of the wave vector of photoelectrons parallel to the surface), we combined the data of several consecutive measurements as a simple linear combination in the region of overlap without further intensity normalization. The estimated resolutions are less than 30 meV for kinetic energy and less than 0.01 Å⁻¹ for k∥.

3. Results and discussion

The photoemission from Al(1 0 0) along the high-symmetry lines, Ì and ÏM, in the surface Brillouin zone was measured with many photon energies. Fig. 1 displays representative results measured with photon energies 54 eV [Fig. 1(a) and (b)] and 45 eV [Fig. 1(c) and (d)]; the photoemission along Ì with photon energy 50 eV is shown in Fig. 3(a). Plotted against the binding energy and k∥, the photoemission intensity is normalized independently in each figure and illustrated with varied color; white marks the greatest and black the least intensity. Fig. 1(b) covers a range of binding energy wider than the others. The regions enclosed with green dashed lines indicate the projected bulk band gap. Many features are readily identified with lines of lighter colors. The origins of these features might be either surface- or bulk-related; they are discerned on comparing the photoemission measured with varied photon energy. The binding energy of surface-related features remains constant whereas the binding energy of the bulk-related features might vary with the photon energy [7]. The photoemission intensity of an electronic state can be significantly modulated by several factors, such as the photon–energy dependent photoionization cross section and the polarization of the incident photons. To identify the surface states properly, one must measure the photoemission with varied photon energies.

Three surface states are identified and denoted as S1, S2, and S3 in Fig. 1. The dispersions of these surface states were determined by analyzing each curve of energy distribution. Plotted as the black dots in Fig. 2, the dispersions are nearly free-electron-like, and their effective masses are determined on fitting them to second-order polynomial functions; the fitted results are shown as the yellow solid lines in Fig. 2. In Fig. 2(b), the dispersions are modulated because of the avoided crossing between the dispersions; only the data close to Ì (for S1) and Ì (for S2) are included in the fitting. The detailed dispersions of the Al(1 0 0) surface states were reported in the previous theoretical studies [3, 4]; the result published in Fig. 8 of Ref. [4] is plotted as the blue dashed lines in Fig. 2 for comparison. Our photoemission results agree qualitatively with this theoretical result with the noticeable deviation in the binding energies.

3.1. Surface band structure along ÌX

Figs. 1(b), (d), 2(b), and 3(a) show the photoemission results along ÌX. Two surface states, S1 and S2, are identified. The binding energy of the broad feature on the upper right side varies with photon energy, demonstrating its bulk-related nature. According to preceding works, S1 is centered at Ì and follows a nearly
free-electron-like dispersion toward the Fermi level [1, 2, 7, 8]. As shown in the figures, part of $S_1$ resides outside the projected bulk band gap, agreeing with the observations of preceding authors. Analysis of the dispersion in Fig. 2(b) yields that, at $\Gamma$, $S_1$ has binding energy $2.80 \text{ eV}$ below the Fermi level and effective mass $1.07 m_e$; $m_e$ is the rest mass of a free electron. The measured binding energy agrees with the reported experimental ($2.8 \pm 1$ and $2.75 \pm 0.17 \text{ eV}$) [2, 7] and the calculated values ($2.65-2.59 \text{ eV}$) appeared in Table II of Ref. [3]. Our effective mass deviates slightly from $1.03 m_e$, reported by Gartland and Slagsvold [1] and 1.18 $m_e$ reported by Levinson et al. [7]; Levinson et al. determined the effective mass on analyzing the $S_1$ dispersion published by Gartland and Slagsvold [1] and Hansson and Flodström [2]. The angular resolution, directly related to the resolution of $k_h$, in their measurements ($8^\circ$ [1, 2]) is worse than ours ($0.125^\circ$). These disparate angular resolution and accuracy of the measurements readily account for the small discrepancy in the effective mass.

$S_2$ is less studied than $S_1$. Predicted theoretically, $S_2$ locates within a narrow band gap centered at $X$ [3, 4]. The only published experimental datum on $S_2$ is its binding energy, determined approximately in a tedious measurement of off-normal photoemission: cf. Fig. 16 in Ref. [7]. Experimental evidence on $S_2$ is lacking likely because of the limited capability of traditional electron energy analyzers. With the improved angular resolution and sampling accuracy offered by a contemporary analyzer, the dispersion of $S_2$ is readily measured. The photoemission intensity of $S_2$ is much less than that of $S_1$, and might be almost undetectable if measured with inappropriate photon energies [7, 9]. According to analysis of data in Fig. 2(b), $S_2$ is centered at $X$ with binding energy $4.62 \text{ eV}$ and has a nearly free-electron-like dispersion with effective mass $0.35 m_e$. This binding energy is within the range of calculated values ($4.48-4.71 \text{ eV}$) compiled in Table II of Ref. [3], and is slightly larger than the experimental value $4.55 \text{ eV}$ [7]. This small disagreement likely results from the much improved angular resolution and accuracy of our experiment.

The results in Figs. 1(b), (d), and 3(a) all show an apparent discontinuity in the $S_1$ dispersion at $k_h \sim 0.55 \AA^{-1}$. Hansson and Flodström observed a “mixing in the shape of the spectra” within a narrow angular interval, and suggested that it resulted from $S_1$ crossing the band edge along $\Gamma X$ [2]; their suggestion is doubtful because no such behavior is observed when $S_1$ crosses the band edge along $\Gamma M$. Our result indicates that the discontinuity locates where $S_1$ and $S_2$ intersect, and the dispersion near the discontinuity resembles the avoided crossing between $S_1$ and $S_2$: this avoided crossing is particularly evident in Fig. 3(a), in which $S_2$ continues to disperse all the way to the Fermi level after it intersects with $S_1$. This avoided crossing between the surface states was predicted theoretically [3, 4], but remained unconfirmed experimentally. Fig. 3(a) shows the photoemission of Al(1 0 0) along $\Gamma X$ measured with photon energy $50 \text{ eV}$. Several energy distribution curves (EDC) cutting through the region of the avoided crossing are plotted in Fig. 3(b); their emission angles are indicated with the spectra. The green dashed line in Fig. 3(a) indicates the binding energy and $k_h$ explored on measuring the EDC at emission angle 9.525°. Two energy states evolving in a fashion of an avoided crossing are observed in Fig. 3(b). By fitting each spectrum with two lines, we found the energy gap of width $0.20 \text{ eV}$ associated with the avoided crossing centered at 1.63 eV below the Fermi level.

3.2. Surface band structure along $\Gamma M$

Fig. 1 (a) and (c) shows the photoemission results along $\Gamma M$. We investigated the photoemission with varied photon energy, and identified two surface states, $S_1$ and $S_3$: their dispersions are plotted in Fig. 2(a). Similarly to the result along $\Gamma X$, $S_1$ is centered at $\Gamma$ and follows a nearly free-electron-like dispersion toward the Fermi level. Analyzing the dispersion in Fig. 2(a) yields $1.07 m_e$ for its effective mass at $\Gamma$, similar to $\Gamma M$, the same as that along $\Gamma X$: $S_1$ is hence isotropic near $\Gamma$. Although $S_1$ crosses the band edge into the symmetry gap at $k_h \sim 0.74 \AA^{-1}$, no discontinuity in the $S_1$ dispersion is observed, in agreement with previous observations [2, 10]. According to the theoretical predictions, the discontinuity in the $S_1$ dispersion along $\Gamma M$ caused by the intersection between the surface states exists above the Fermi level [3, 4], but was not investigated because the photoelectron spectroscopy employed in this study explored only the filled electronic states.

The surface state $S_3$ was predicted to disperse inside the symmetry gap over the range $0.9-1.4 \AA^{-1}$ of $k_h$ along $\Gamma M$ [3, 4, 11], but was not observed previously. Our result in Fig. 2(a) indicates that $S_3$ disperses over the range $1.1-1.4 \AA^{-1}$ of $k_h$, with maximum binding energy $0.82 \text{ eV}$ at $k_h \sim 1.2 \AA^{-1}$; its dispersion is nearly free-electron-like with effective mass $0.52 m_e$. Our result agrees qualitatively with the theoretical predictions apart from notable discrepancies. As shown in Fig. 2(a), the measured binding energy is $0.25 \text{ eV}$ higher than the theoretical value. In addition, $S_3$ is missing over range $0.9-1.1 \AA^{-1}$ of $k_h$. The reason for this discrepancy is uncertain but might be partly understood from the data in Fig. 4.
shows raw data in two consecutive photoemission measurements, of which the emission angles of photoelectron partially overlap. Inside this overlap region, there is no sign of $S_2$ in Fig. 4(a), but $S_2$ is clearly observed in Fig. 4(b). This peculiar behavior is independent of photon energy, and might have played a role in the result published by Jiang et al. in which $S_2$ was missing completely [10]. As described in Section 2, to accomplish the measurements in Fig. 4, one must rotate the sample. The only variation between the two measurements is the sample orientation relative to the polarization of the incident light. The intensity distribution of photoemission is variable with the polarization of the incident light, which was not adjustable in this study. Further investigations are required to clarify this issue.

3.3. Electron–phonon coupling of $S_1$ at $\bar{\Gamma}$

The surface state $S_1$ has been investigated as a model system to investigate the interaction between electrons and photons at a metallic surface. The calculated electron–phonon coupling strength (\(\lambda\)) of $S_1$ at $\bar{\Gamma}$ varies over a range 0.23–0.51 [9,12,13]. The lack of a reliable experimental value for \(\lambda\) of $S_1$ at $\bar{\Gamma}$ motivated our investigations. One common method to evaluate \(\lambda\) of an electronic state is a measurement of the temperature dependence of its line width. At the limit of high temperature, the line width (\(\Delta E\)) of the electronic state depends linearly on temperature (\(T\)); \(\lambda\) is determined by the expression \(\Delta E/\Delta T = 2\pi k_B \lambda\), where \(k_B\) is the Boltzmann’s constant [14]. We annealed slowly the Al(100) surface from 90 to 420 K while measuring concurrently the photoemission of $S_1$. Fig. 5(a) shows the representative EDC of $S_1$ at $\bar{\Gamma}$ at various temperatures; the spectra are shifted vertically without normalization. The line width of $S_1$ increases as temperature increases. The binding energy of $S_1$ remains constant during the annealing, in contrast with the surface states of noble metals [15]. To determine the line width of $S_1$, each spectrum was fitted with a sum of a polynomial background and a Voigt function with the Gaussian width (full width at half maximum, FWHM) fixed to the instrumental resolution (30 meV); the results from the fit are plotted as the red lines in Fig. 5(a). The Lorentzian width (FWHM) from the best fit was assigned as the line width of $S_1$. This width is plotted against annealing temperature in Fig. 5(b), showing the linear dependence of line width on temperature. The result from linear regression of the line width, plotted as the gray solid line, yields \(\lambda = 0.59\) for $S_1$ at $\bar{\Gamma}$, disagreeing with 0.23 from an early calculation [12] but agreeing approximately with 0.51 from a recent calculation [13]. Jensen et al. proposed a mechanism for the line broadening based on thermally induced defects on Al(100) [9]. The data in Fig. 5(b) show satisfactory linearity, indicating that thermally induced defects on Al(100) are not observed from 90 to 420 K in our experiment.

3.4. ARPES with two-dimensional electron detection

Many long predicted features of the surface band structure of Al(100) are confirmed experimentally in this work. The key element to our success is the electron energy analyzer with a two-dimensional channel plate and an electron lens of adequate angular resolution, which became accessible only since 2000. The complication of measuring ARPES in an off-normal direction is illustrated in Fig. 3. In Fig. 3(b), each spectrum is regarded as an EDC in one traditional photoemission measurement with the specified emission angle and photon energy. Measured with photon energy 50 eV, the energy gap in the $S_1$ dispersion is identified in only a few EDCs within an interval 0.5\(^\circ\) of emission angle. Working with a traditional electron energy analyzer, to have an EDC cutting through the desired electron energy-momentum space, one must specify accurately both the photon energy and the emission angle. Furthermore, exploring unknown off-normal features in the surface band structure requires scanning the electron energy-momentum space with correct combinations of photon energy and emission angle. As this process is tedious, it is likely the major reason for the scarcity and poor quality of off-normal photoemission measurements before present analyzers became available. Our results indicate that to reinvestigate some previously studied systems with present photoemission instruments of the good angular resolution and sampling accuracy is worthwhile.

4. Summary

From high-resolution ARPES measurements on the Al(100) surface, we identified three surface states: $S_1$ is centered at $\bar{\Gamma}$ with binding energy 2.80 eV and effective mass 1.07\(m_e\); $S_2$ is centered at $\bar{X}$ with binding energy 4.62 eV and effective mass 0.35\(m_e\); $S_3$ is observed over range 1.1–1.4Å\(^{-1}\) of \(k\) along $\bar{\Gamma}M$ with the maximum binding energy 0.82 eV and effective mass 0.52\(m_e\) at $k = 1.20Å\(^{-1}\) Along $\bar{\Gamma}K$, $S_1$ and $S_2$ intersect at $k = 0.55Å\(^{-1}\)$ and the avoided crossing between $S_1$ and $S_2$ is observed; the resulting energy gap of width 0.2 eV is centered at binding energy 1.63 eV. The electron–phonon coupling strength of $S_1$ at $\bar{\Gamma}$ is 0.59. No thermally induced defect on Al(100) is observed from 90 to 420 K. Our
work provides experimental data to serve as reference for future investigations.

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