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Reinvestigation of the band structure of the Si(111)5×2-Au surface

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The electronic band structure of the Si(111)5×2-Au surface is reinvestigated in detail by angle-resolved photoelectron spectroscopy (ARPES), especially for the surface-state bands near the Fermi energy. Through extensive ARPES measurements and analyses, four different surface-state bands are identified within the bulk band gap, the dispersions of which are determined. It was clearly shown that the Si(111)5×2-Au surface is semiconducting at room temperature with a band gap larger than ~0.2 eV in contrast with previous ARPES results. Furthermore, the band dispersions determined are not compatible with a Peierls-gap idea proposed recently.

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INTRODUCTION

Nanostructures or low-dimensional structures generated by metal adsorption on semiconductor surfaces exhibit a variety of exotic physical phenomena and have attracted considerable interest in recent years both academically and technologically. There have been reports of charge-density waves in two-dimensional[1–4] (2D) and quasi-one-dimensional[5] (quasi-1D) systems, spin-charge separation in metallic chains,[6] metallic umklapp bands arising from a discommensurate overlayer,[7] and enhanced surface conductivity via adatom doping.[8]

One of the important current issues is the electronic structures of the 1D metallic Au/Si systems, especially the Si(557)-Au and Si(111)5×2-Au surfaces. The Si(557)-Au surface prepared by ~0.2 ML Au adsorption on Si(557) is composed of 1D chains and has two narrowly spaced bands near the Fermi level (E_F).[6,9] It has been argued to attribute these two states to a spinon-holon pair, as in a Luttinger liquid,[6] or to two different electronic states related to the different chain structures within a unit cell.[9]

On the other hand, a similar 1D chain structure of Si(111)5×2-Au, prepared by ~0.4 ML Au on Si(111),[10–19] shows a variety of surface-related valence-band features indicating the complicated nature of its electronic structure.[10] This surface was suggested to be a generic quasi-1D metallic system in an early angle-resolved photoelectron spectroscopy (ARPES) study.[13] However, in spite of a rather strong and anisotropic photoemission signal near E_F (denoted S_1 state hereafter), no clear evidence for E_F crossing was found in a later inverse photoemission study.[15] Recent high-resolution ARPES work on this surface at a very low temperature also observed a similar state very close to E_F (probably identical to S_1),[11] but they identified another surface-state band approaching E_F with a strong dispersion from a binding energy (E_B's) of ~1.3 eV (denoted S_2 hereafter).[10,12] This band was reported to exhibit a band gap of larger than ~0.3 eV at low temperature due to the Peierls instability.[10–12] The same group further reported that the density of states at E_F increases as the surface is warmed to room temperature, suggesting a pseudogaplike behavior.[10] This observation makes it very unclear whether the 5×2-Au surface is metallic or not at room temperature and the presence of the S_1 state, closer to E_F, provides more complexity to this issue.

In the present work, we have engaged in an extensive band mapping on the Si(111)5×2-Au surface in order to determine its detailed electronic structure near E_F at room temperature. Four different surface states are identified within the silicon bulk band gap, and their dispersion along the $[10\bar{1}]$ direction (along the 1D chains) was determined in detail. While the overall surface-state dispersions match previous ARPES results[10–13,16] consistently, we found that the surface is semiconducting with a band gap larger than ~0.2 eV. This gap is not due to the S_2 state but due to the S_1 state, which was found to exhibit an almost perfect 1D behavior. The implications of this finding on the Peierls-gap idea and the origins of the surface states[17] observed are discussed.

EXPERIMENTS

The experiments were performed in a modified Vacuum Generator ESCALAB 220 photoelectron spectrometer described elsewhere.[20] The sample was a *p*-type crystal (2–10 Ω cm) and had an intentional miscut of 2° toward $[\bar{1}\bar{1}2]$ in order to obtain a single-domain (SD) Si(111)5×2-Au surface.[10,13–15] The crystal orientation of

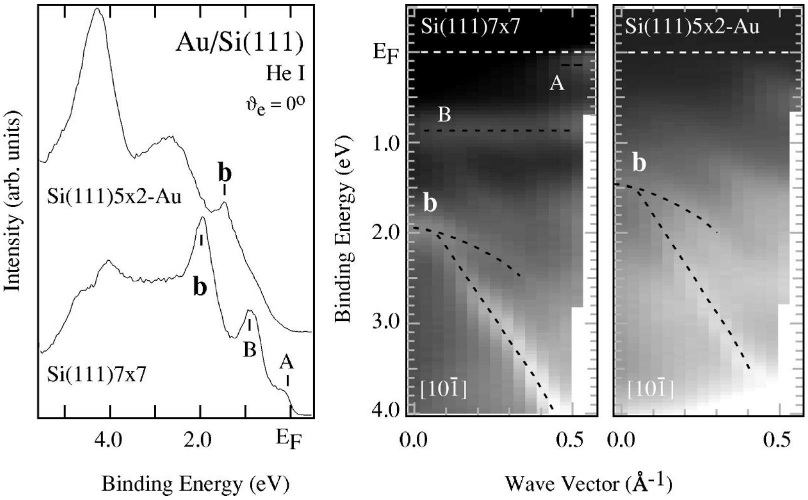

FIG. 1. (left) He I excited normal emission spectra for the Si(111)7×7 and single-domain Si(111)5×2-Au surfaces. A bulk direct transition (**b**) and surface states *A* and *B* of Si(111)7×7 are indicated. (right) Gray-scale E_B-$k_\parallel$ diagram for the Si(111)7×7 and single-domain Si(111)5×2-Au surfaces along $[10\bar{1}]$ taken from the ARPES scans with the He I excitation.

the sample was determined from x-ray photoelectron diffraction measurements to within better than 1°. Gold was evaporated from a hot tungsten filament with the pressure being kept below 5×10^{-10} mbar during deposition. The evolution of the low-energy electron diffraction (LEED) pattern during Au deposition at different coverages and substrate temperatures were the same as reported previously.[14] A SD Si(111)5×2-Au surface, as judged from the well-defined LEED pattern, was formed by a deposition of ~0.4 ML of Au at $\sim600\,^\circ$C as reported before.[10,13–15]

For the photoemission measurements, He Iα (21.2 eV) and He IIα (40.8 eV) radiation were used for excitation, produced in a microwave-driven high-flux He discharge lamp with a toroidal grating monochromator (Gammadata Burklint AB, Sweden). The energy resolution of the electron analyzer was set to about 40 meV and the angular resolution to better than 1° full width at half maximum. Data acquisition was made either by taking series of energy spectra while scanning the photoelectron emission angles (polar or azimuthal angle) to produce energy dispersion plots or by recording the photoelectron intensity at constant energy as function of both emission angles across the full hemisphere to produce constant-energy surface maps.[20] The Fermi energy was determined by fitting the Fermi edge in spectra from polycrystalline silver and from a Ta plate attached to the Si wafer. A work function of 4.67 ± 0.08 eV was determined from the low-energy cutoff of the photoemission spectra. All the experiments were performed at room temperature (RT) with a base pressure below 8×10^{-11} mbar.

RESULTS AND DISCUSSION

For band mapping experiments on semiconducting samples, the determination of the projected bulk band structure or valence-band maximum (VBM) is important for identifying the bulk band gap where surface states exist. In order to determine the VBM unambiguously, we performed ARPES measurements along $[10\bar{1}]$ for clean Si(111)7×7 and Si(111)5×2-Au surfaces that show the clear dispersions of bulk bands. The prominent ARPES signal denoted as **b** in Fig. 1 is due to the Si bulk states. It is obvious that the bulk state **b** is shifted to a lower E_B by ~0.5 eV for Si(111)5×2-Au as compared with Si(111)7×7. Since the position of the VBM with respect to E_F is firmly established for Si(111)7×7,[21,22] the present data yield a VBM position of ~0.1 eV below E_F for Si(111)5×2-Au. This quantity is crucial for the issue of the proposed Peierls-transition picture for the surface[10,12] as described below.

Figure 2 shows series of ARPES spectra taken with He I along the $\overline{\Gamma}_0$-$\overline{X}_0$ and $\overline{\Gamma}_3$-$\overline{X}_3$ surface Brillouin zone (SBZ) lines at RT. The SBZ is shown in Fig. 2 together with symbols of zone boundaries, $\mathrm{ZB}_{\times2}$, $\mathrm{ZB}_{\times1}$, and $\mathrm{ZB}'_{\times2}$. As indicated in these spectra, a surface state (S_1) can be identified near E_F in the vicinity of $\mathrm{ZB}_{\times2}$ ($\mathrm{ZB}'_{\times2}$) along both SBZ lines. This state was also observed in a previous ARPES studies by Collins *et al.*,[13] Okuda *et al.*,[16] and recently by Himpsel *et al.*[11] We can also identify other states, labeled S'_3, S_3, and S_4, in the energy range of 0.5–1.5 eV as shown in the figure. Using He II excitation, yet another state labeled S_2 appears as an intense peak, as can be seen in Fig. 3. The state S_2 was observed in recent ARPES measurements by Losio and co-workers.[10,12] That result, especially the dispersion of S_2, is fully consistent with the present one except for the different peak intensities, which may be due to the different photon energies employed. The S_2 state is hardly identified with He I excitation, as shown in Fig. 2, which would have made the earlier ARPES studies unable to identify this state.[13,16] In Fig. 3, we observe the S_1, S_3, and S_4 states with the same dispersion as in Fig. 2. All the above states are considered to be surface states because they disperse within the bulk band gap (as shown below) and their dispersion does not change with respect to the excitation energy.

We will focus now on the state closest to E_F, S_1, since it governs the electronic properties (i.e., being metallic or not) of the Si(111)5×2-Au surface. As rather obviously noticed in the figure, no clear Fermi edge is detected throughout the whole SBZ. A closer look of the spectra near E_F is provided in Fig. 4. Here S_1 does not cross E_F apparently but is backfolded around the middle of $\mathrm{ZB}_{\times1}$ and $\mathrm{ZB}_{\times2}$, making the Si(111)5×2-Au surface semiconducting. From the apparent peak positions, the lowest E_B of S_1 is estimated to be about ~0.2 eV, which should correspond to the size of the band

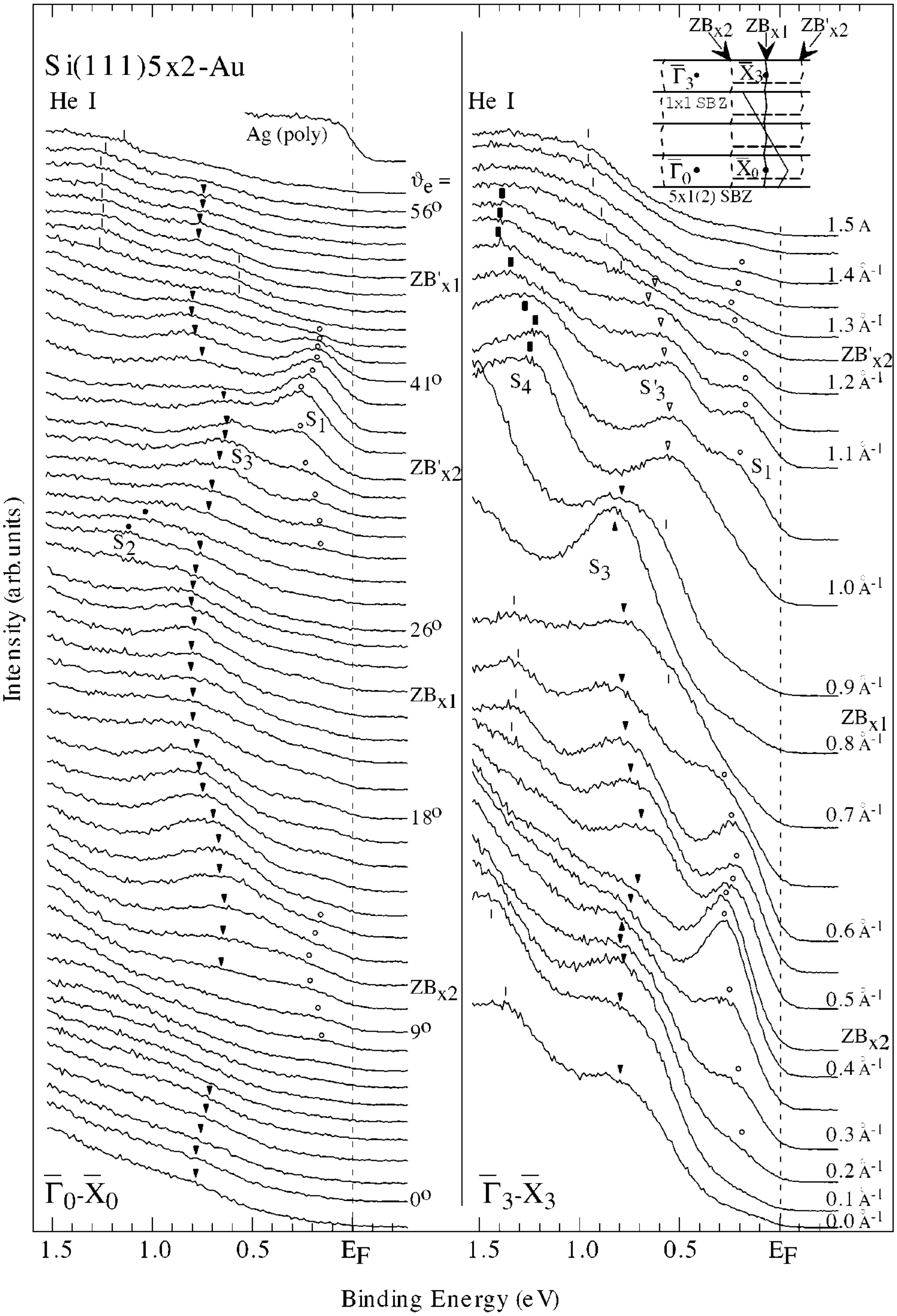

FIG. 2. ARPES spectra for the single-domain Si(111)5×2-Au surface taken with He I along $\overline{\Gamma}_0$-$\overline{X}_0$ and $\overline{\Gamma}_3$-$\overline{X}_3$. The spectra are shown as a function of emission angle (θ_e) or wave vector ($k_{\parallel}$). Zone boundaries (ZB's) and symmetry points in the Si(111)-(5×2) surface Brillouin zones are also indicated. $\mathrm{ZB}_{\times 2}$ ($\mathrm{ZB}'_{\times 2}$) and $\mathrm{ZB}_{\times 1}$ correspond to the boundaries of the 5×2 and 5×1 unit cells, respectively. Positions of peaks assigned to different surface state bands (see the text) are marked with different symbols. A spectrum of polycrystalline Ag is also shown. The dashed lines correspond to energy levels for the contours in Fig. 6.

gap below E_F. This result is in conflict with a few previous ARPES results[11,13] but agrees with an inverse photoemission study.[15] In order to corroborate the semiconducting nature of S_1, we have also considered ARPES spectra as normalized by the Fermi-Dirac function.[23] This is because there is marginal but still nonzero photoemission intensity right at E_F, which is presumably due to the thermal (Fermi-Dirac) excitation and finite instrument resolution. Figure 4 compares the raw and Fermi-Dirac-function-normalized spectra around $\mathrm{ZB}'_{\times 2}$ and $\mathrm{ZB}_{\times 2}$ at the vicinity of E_F. Both types of spectra show that the intensity at E_F is trivial and structureless. These data indicate again that S_1 never crosses E_F; note the discernible dispersion of the peak for the band backfolding. We have further applied an established analysis procedure in order to extract the density of states at E_F (or the band gap) quantitatively.[24] Briefly, the energy scale of a measured spectrum is reflected at E_F and the spectrum is added to the original one. This procedure yields $I(E)=I(E-E_F)+I(E_F-E)$ where I is photoemission intensity. Each peak appears, thereby, twice (below and above E_F) and both should merge into one when the state crosses E_F. Even in this analysis, no trend of the gap narrowing and no sign of an E_F crossing were observed, giving further evidence for a semiconducting surface.

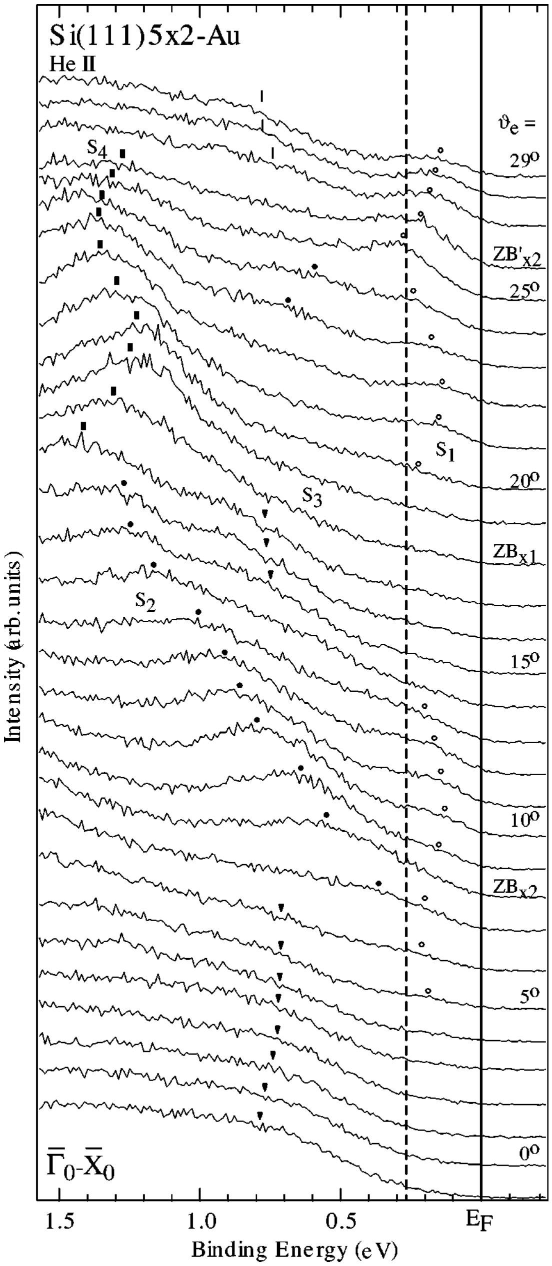

FIG. 3. Similar to Fig. 2 but for He II excitation along the $\overline{\Gamma}_0$-$\overline{X}_0$ direction. The dashed lines correspond to energy levels for the contours in Fig. 6.

We now turn to a comprehensive determination of the band dispersions of the various surface states observed. Figure 5 shows the experimental dispersion curves for the spectral features observed along the $\overline{\Gamma}_0$-$\overline{X}_0$ and $\overline{\Gamma}_3$-$\overline{X}_3$ lines in the 5×2 SBZ shown in Fig. 2. The data were taken with He I (solid circles for the $\overline{\Gamma}_0$-$\overline{X}_0$ line and open circles for the $\overline{\Gamma}_3$-$\overline{X}_3$ line) as well as He II excitation (solid squares for the $\overline{\Gamma}_0$-$\overline{X}_0$ line). For the ARPES scans taken with He II excitation, the gray-scale $E_B-k_\parallel$ diagram ($k_\parallel$, the wave vector component parallel to the surface) is also shown in the figure, where the photoemission intensity is plotted with respect both to E_B and $k_\parallel$. The shaded region in the lower figure is the bulk band projected onto the 1×1 SBZ.[21] The position of the bulk VBM is accurately determined as shown in Fig. 1. All the bands S_1, S_2, S_3, S_3', and S_4 have parts of their dispersion curves within the projected bulk band gap, indicating their surface nature. The overall dispersion curves are found to be consistent with most of previous ARPES results[10,12,13,16] except for a few important details as mentioned above for S_1 and as discussed further below. Very recently, *ab initio* band calculations[17] were performed for the available structure models of the 5×2-Au surface proposed by Hasegawa *et al.*[18] and Marks *et al.*,[14] respectively. Both models, however, yield surface band structures, which are not in accordance either with previous or with the present ARPES data, especially within the bulk band gap. While this discrepancy indicates the need of a different or a refined structure model for the surface, the calculation has shown that surface states within the band gap originate mostly from Si 3*p* (dangling bond or back bond) states.[17]

We then go back to the S_1 state, which is crucial for determining the electronic properties of the surface. In order to study the band dispersion of this state in more detail, we have performed constant-energy surface mapping at $E_B=0.26$–0.27 eV. As guided by the dashed lines in Figs. 2, 3, 4, and 5, the constant-energy contours at this energy represent the photoemission intensity distribution of the S_1 state. Figure 6 shows the resulting constant-energy contours, as obtained with He I and He II photons, as function of $k_\parallel$. The photoemission intensity is represented in a gray scale where the bright part corresponds to high photoemission intensity. The SBZ of the 1×1 and 5×1 unit cells as well as ZB's of the 5×2 unit are displayed as thick solid, thin solid, and dashed lines, respectively. It is notable that the photoemission intensity is distributed as parallel straight lines along k_y in every image. The extra intensity variations along each straight lines or between different lines can be attributed to the photoemission matrix element effects[25,26] and/or the distribution of spectral weight between umklapp bands in different BZ's.[7] The constant-energy contours composed of straight lines clearly indicate that the S_1 band has almost perfect 1D dispersion along the $\overline{\Gamma}_0$-$\text{ZB}_{\times2}$-$\text{ZB}_{\times1}$ line (k_x)—that is, no dispersion along k_y. Note that the $\overline{\Gamma}_0$-$\text{ZB}_{\times2}$-$\text{ZB}_{\times1}$ line is along the 1D chain structure of the Si(111)5×2-Au surface.

Previously, it has been argued that the photoemission signals near E_F (presumably corresponding to S_1 of the present work) may originate from the surface states of Si(111)7×7 or Si(111)$\sqrt{3}\times\sqrt{3}$-Au that may coexist on the Si(111)5×2-Au surface.[12] However, the lack of threefold symmetry and the 1D dispersion shown above allows the S_1 state to be undoubtedly assigned to an intrinsic feature of Si(111)5×2-Au. This assignment is important since that previous study interpreted the band top of S_2 as the band gap of the Si(111)5×2-Au surface itself, which is obviously misleading when we consider the S_1 state. Note that the band gap determination in terms of the S_2 state led to the idea of Peierls gap formation from a half-filled 1D band.[10,12] Moreover the spectral weight in angle-integrated photoemission spectra at RT was interpreted as the possible sign of a pseudogap.[10] The present data obviously show that the pho-

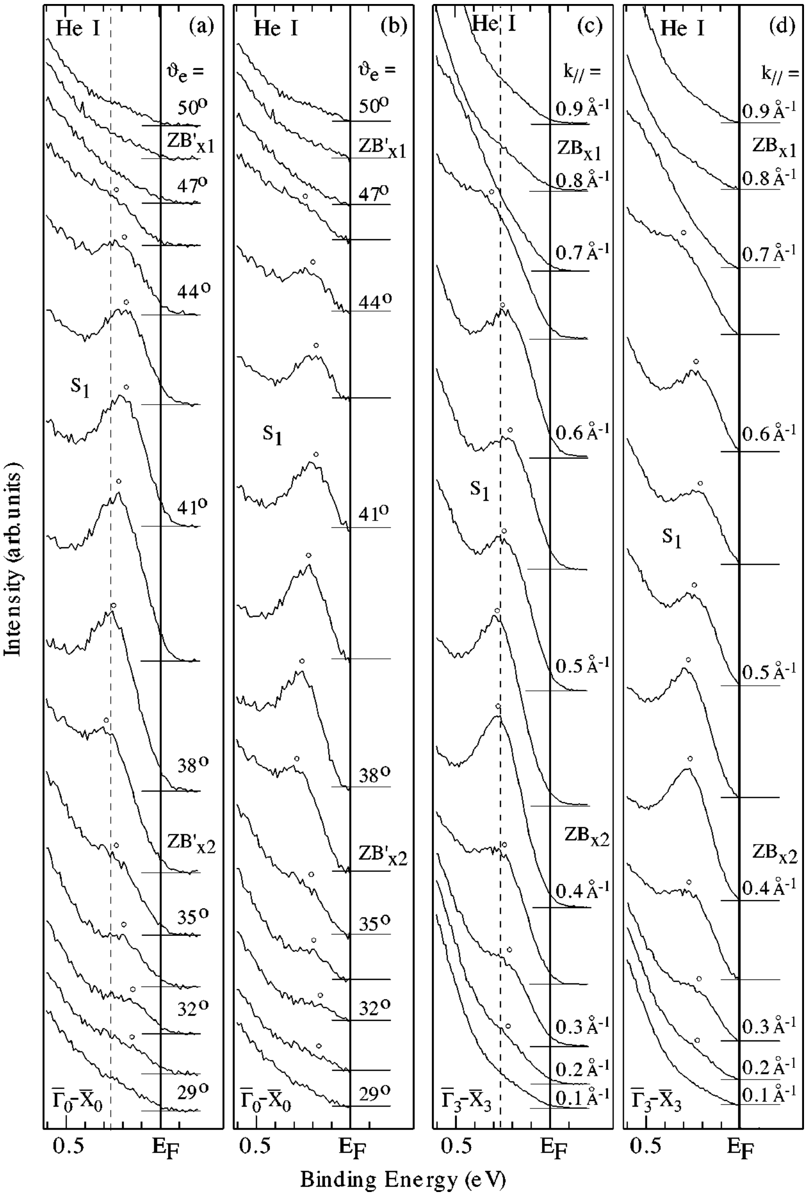

FIG. 4. ARPES spectra near E_F for the Si(111)5×2-Au surface taken with He I excitation. (a) and (b) are raw and Fermi-Dirac function normalized spectra taken along $\overline{\Gamma}_0$-$\overline{X}_0$, respectively, while (c) and (d) are those along $\overline{\Gamma}_3$-$\overline{X}_3$. The dashed lines correspond to energy levels for the contours in Fig. 6.

toemission intensity near E_F is due to the S_1 band, which is intrinsic to the Si(111)5×2-Au surface, and the band gap of the surface is governed not by S_2 but by S_1. It is notable that both S_1 and S_2 possess strong 1D characteristics. Moreover, since the band gap of S_1 occurs quite far away from the ×2 zone boundary, the Peierls-gap idea is not valid at all. Then, the gap of the S_2 band at $\text{ZB}_{\times 2}$ can be explained by a simple band picture of a splitting between S_1 and S_2 (an anticrossing behavior).

As shown in Fig. 5, the determination of the bulk VBM is important in identifying a surface state. This is more important for low-temperature photoemission measurements where the surface photovoltage effect shifts the Fermi level of the surface, making the determination of the metallicity or the band gap uncertain. Indeed, the low-temperature ARPES study discussed above mentioned such an uncertainty for the determination of the band gap of the S_2 state.[12] This study assumed the VBM position at 0.3 eV below E_F but an earlier core-level study reported it to be 0.1 eV.[27] As shown in Fig. 1, the present work yields a VBM position of ~0.1 eV below E_F for Si(111)5×2-Au. This confirms the previous determination of Okuda *et al.*[27] and corrects the band top position of S_2 being ~0.4 eV from E_F and ~0.3 eV below the VBM (see Fig. 5). We believe that such an uncertainty in the E_F position for the low-temperature measurement causes a discrepancy in the semiconducting nature of the S_1 state.[11]

CONCLUSIONS

We have performed detailed band mapping measurements by angle-resolved photoemission spectroscopy to study the room-temperature electronic structure of the Si(111)5×2-Au surface, which is composed of a 1D chain structure. Through extensive ARPES measurements for different SBZ lines, we have identified the presence and dispersions of at least four different surface state bands S_1, S_2, S_3,

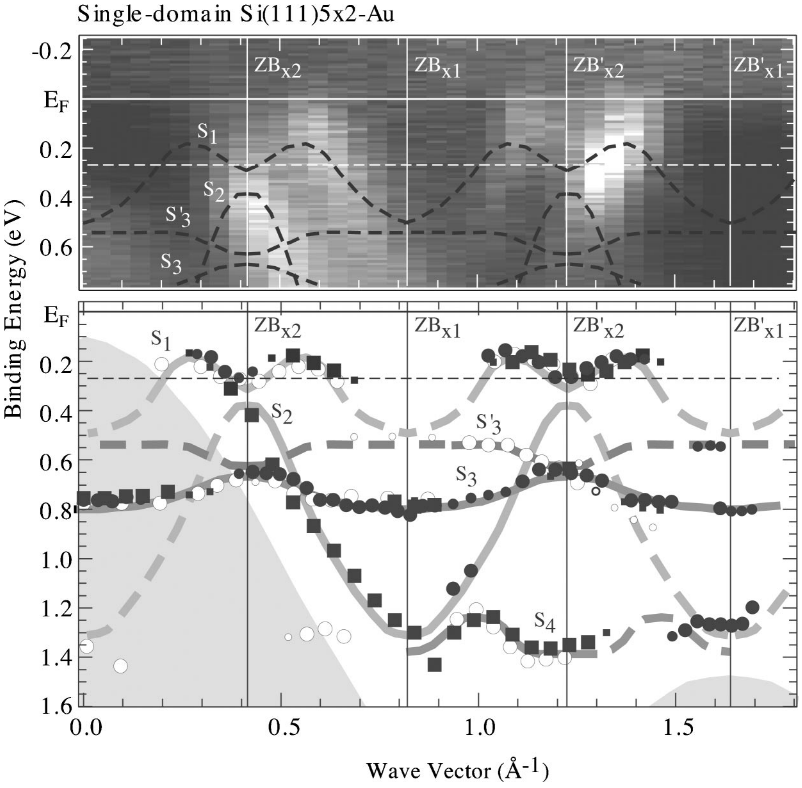

FIG. 5. (upper) The gray-scale E_B-$k_\parallel$ diagram for the single-domain Si(111)5×2-Au surface along the $\overline{\Gamma}_0$-$\overline{X}_0$ direction taken from the ARPES scan with He II excitation. In the diagram, the intensities are represented by the brightness, white corresponding to high intensity. The dispersions for the surface states are depicted by black dashed curves. The white dashed lines correspond to the energies where the contours of Fig. 6 were taken. (lower) Experimental dispersions for the single-domain Si(111)5×2-Au surface along the $\overline{\Gamma}_0$-$\overline{X}_0$ direction. Large and small symbols represent rather distinctive and weak spectral features, respectively. Solid circles (squares) indicate peak positions obtained with the He Iα (He II) excitations. Peak positions taken along the $\overline{\Gamma}_3$-$\overline{X}_3$ direction with the He Iα excitation are also shown as open circles. The shaded region is the bulk band structure projected onto the 1×1 surface Brillouin zone. The major surface state bands are traced by thick gray curves.

and S_4 within the bulk band gap. These states are shown to be intrinsic to the Si(111)5×2-Au surface, and the S_1 band close to E_F is found to have a 1D dispersion along the chains. The surface at room temperature is unambiguously shown to be semiconducting with a band gap larger than 0.2 eV, which is due to the S_1 band. This result clearly denies the Peierls-gap picture proposed recently for this surface at a low temperature.

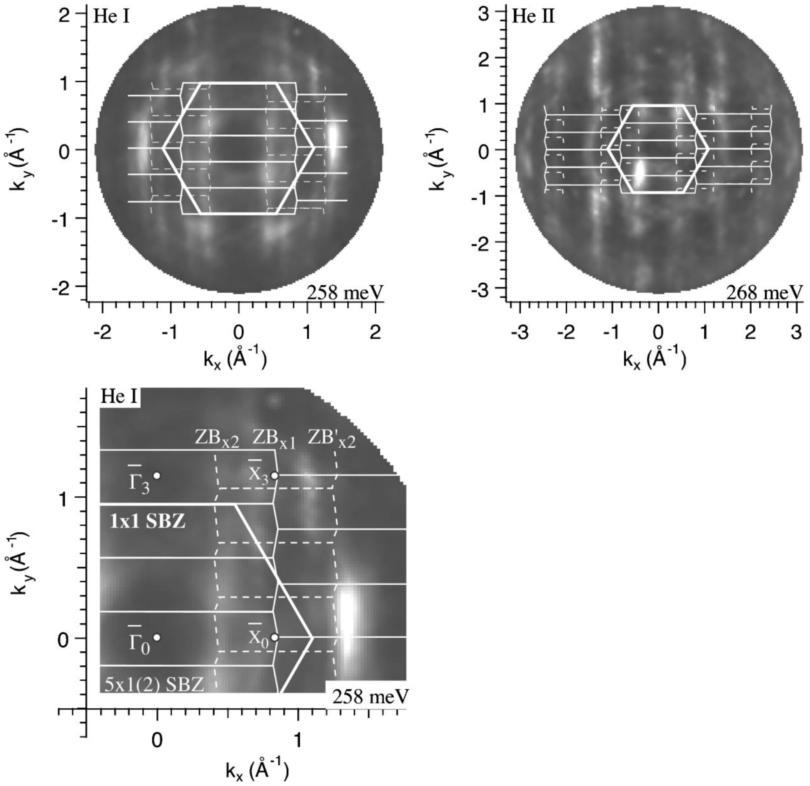

FIG. 6. He I and He II excited photoemission energy contour maps from the Si(111)5×2-Au surface. In each image, the photoemission intensity at the indicated binding energies is mapped as a function of wave vector parallel to the surface in linear gray scale. The magnified image is shown for the image taken at a binding energy of 258 meV. The Si(111)-(1×1) surface Brillouin zones (SBZ's) are added as white bold lines. The Si(111)-(5×2) SBZ's are shown as thin dashed lines (zone boundary, ZB$_{\times 2}$) and thin solid lines (ZB$_{\times 1}$) together with high-symmetry points.

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