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Electronic structure of the Ca/Si(111)-(3×2) surface

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The electronic structure of the Ca/Si(111)-(3×2) surface has been investigated by angle-resolved photoelectron spectroscopy. Five surface states, none of which crosses the Fermi level, were observed in the bulk band gap, and one surface state was observed in a bulk band pocket. The dispersion features of three of the surface states in the band gap agree well with results from monovalent atom adsorbed Si(111)-(3×1) surfaces along the chain direction. The close resemblance indicates that the origins of the surface states are the same as or quite similar to those of the (3×1) surface. The two other states observed in the band gap have not been reported in the literature, and they are interpreted as surface states that occur on Ca/Si(111)-(3×2) due to the lower coverage (1/6 monolayer of Ca). Further, based on the finite surface state dispersion in the direction perpendicular to the Ca chains, we conclude that the electronic character of this surface is not completely one dimensional.

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I. INTRODUCTION

One-dimensional (1D) superstructures, which are formed on semiconductor surfaces by the adsorption of metal atoms, exhibit various exotic physical phenomena.^{1–6} The observations of these exciting physical phenomena led to a profound interest in measuring the electronic structures of alkaline-earth metal (AEM) induced Si(111)-(3×2) surfaces, since these surfaces have been proposed to be strongly correlated electron systems.^{7,8} This proposition was based on the assumption that the geometric structure and adsorbate coverage of these surfaces are completely the same as those of alkali metal (AM) induced Si(111)-(3×1) surfaces, i.e., the structure is described by the honeycomb-chain-channel (HCC) model^{9–11} shown in Fig. 1(a). The HCC structure with an AEM adsorbate coverage of 1/3 monolayer (ML) leads to an odd number of valence electrons in a (3×1) unit cell, and the semiconducting electronic structure is unexpected within a simple one-electron description. The observations of ×2 periodicities in the chain direction^{8,12–15} supported the proposition that the semiconducting character results from a Peierls instability with the formation of a charge-density wave.

However, recently, a different structural model, which removes the basis for the above assumption, was proposed by analyzing the scanning tunneling microscopy (STM) image of a Ba/Si(111)-(3×2) surface using an *ab initio* calculation.¹⁶ Figure 1(b) shows this model, whose basic structure is the same as that of the HCC model but with an adsorbate coverage of 1/6 ML. According to this model, the number of valence electrons in the unit cell becomes even, and the semiconducting electronic character can be explained without involving correlation effects. Among the other AEM induced (3×2) surfaces, the Ca/Si(111)-(3×2) surface was reported to have the same geometric structure as the Ba induced surface.^{17–19} So far, three studies have reported the electronic structure of this surface, and a basic understanding is important in order to obtain a complete comprehension of the metal atom induced HCC structure.^{8,18,19} However, these

studies cover only a part of the surface Brillouin zone (SBZ), and the results are not consistent. Two of them reported the observation of two surface states in the bulk band gap,^{8,18} while three surface states were observed in the third study.¹⁹ Further, although it was reported that the interaction between neighboring AEM chains is negligible and the AEM induced Si(111)-(3×2) surfaces have 1D electronic character,^{18,20} there is no detailed study of the electronic structure perpendicular to the AEM chains.

In this paper, we present detailed angle-resolved photoelectron spectroscopy (ARPES) measurements performed along the $[\bar{1}10]$ and $[11\bar{2}]$ directions of the Ca/Si(111)-(3×2) surface, i.e., the directions parallel and perpendicular to the Ca chains. Among the five surface states observed in the bulk band gap, the dispersions of three of them follow a (3×1) periodicity instead of the (3×2) periodicity observed in low-energy electron diffraction (LEED). The good agreement between the dispersions of these three states and those of the three surface states of monovalent atom adsorbed Si(111)-(3×1) surfaces indicates that their origins are the

FIG. 1. (a) HCC structure of the Si(111)-(3×1) surface with an adsorbate coverage of 1/3 ML. (b) Structural model proposed for AEM adsorbed Si(111)-(3×2) surfaces with an adsorbate coverage of 1/6 ML. The geometric structure of Si atoms in (b) is the same as the HCC structure. Filled circles are metal atoms, which are adsorbed on the T_4 site, and open circles are Si atoms. The dashed lines indicate the unit cell of each surface.

same or quite similar. The two other surface states observed in the band gap were not reported on AM induced Si(111)-(3×1) surfaces. Based on the difference between the 1/3 ML and the 1/6 ML HCC structures, we conclude that these two surface states are peculiar to the AEM induced (3×2) reconstructed surface. In the $[11\bar{2}]$ direction, two surface states with finite dispersions and one with negligible dispersion were observed. This result suggests that the electronic character of this surface is quasi-1D, and thus that the interaction between neighboring Ca chains is not negligible.

II. EXPERIMENTAL DETAILS

The ARPES measurements were performed at beamline 33 at the MAX-I synchrotron radiation facility in Lund, Sweden. Photoemission spectra were obtained using an angle-resolved photoelectron spectrometer and linearly polarized synchrotron radiation at photon energies ($h\nu$) of 21.2 and 17 eV. The total experimental energy resolutions were ~ 50 meV at $h\nu=21.2$ eV and ~ 45 meV at $h\nu=17$ eV, and the angular resolution was $\pm 2^\circ$. A Si(111) sample (n type) with a 1.1° miscut toward the $[\bar{1}\bar{1}2]$ direction was used as a substrate. To obtain a clean surface, we annealed the sample by direct resistive heating following the procedure described in Refs. 21 and 22. After the annealing, a sharp (7×7) LEED pattern was observed, and neither the valence-band spectra nor the Si 2*p* core-level spectra showed any indication of contamination. The Ca/Si(111)-(3×2) surface was prepared by depositing Ca onto a clean Si(111)-(7×7) surface at a substrate temperature of ~ 1000 K. The base pressure was below 4×10^{-11} Torr during the measurements, and below 5×10^{-10} Torr during the Ca evaporation.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the LEED pattern of the Ca/Si(111)-(3×2) surface obtained at 300 K with a primary electron energy of 82 eV. Together with the strong ×3 spots, ×2 streaks are observed in the $[11\bar{2}]$ direction. In contrast to the clear ×2 streaks shown in Fig. 2(a), the ×2 streaks of the Ba induced Si(111)-(3×2) surface were reported to be almost invisible in LEED,^{15,20} although a clear ×2 periodicity was observed using STM.^{16,20} The very low intensity of the ×2 streaks was proposed to originate from a random shift of the Ba chains by half a unit cell without changing the chain structure, i.e., Ba atoms are adsorbed on the T_4 sites with a ×2 periodicity as well as at the adsorption site shown in Fig. 1(b), but a random shift is caused along the chain direction due to a negligible interaction between neighboring Ba chains.²⁰ Further, it was stated that this random shift occurs during the sample annealing and cannot be caused by surface diffusion at room temperature.²⁰

In order to study the interaction between neighboring Ca chains, we cooled down the sample. Figure 2(b) shows the LEED pattern of the Ca/Si(111)-(3×2) surface obtained at 100 K using the same primary electron energy as in (a). Compared with the streaks in Fig. 2(a), some extra spots are

FIG. 2. LEED patterns of the Ca/Si(111)-(3×2) surface obtained with a primary electron energy of 82 eV at (a) 300 and (b) 100 K. ×2 streaks are observed together with strong ×3 spots in the $[11\bar{2}]$ direction in (a), and extra spots that originate from (3×2) and $c(6 \times 2)$ reconstructions are clearly observed in (b).

clearly observed in (b). The extra spots correspond to the half-order spots of (3×2) and $c(6 \times 2)$ reconstructions. The LEED pattern in Fig. 2(b) indicates thus that the surface consists of large (3×2) and $c(6 \times 2)$ domains at 100 K, and the interaction between neighboring Ca chains can therefore not be neglected at this temperature. Further, the comparable intensities of the half-order spots in LEED suggest that the domain sizes of the two reconstructions are quite similar, and thus that the interaction between the second neighboring Ca chains can also not be neglected [the $c(6 \times 2)$ reconstruction is formed by shifting every second Ca chain of a (3×2) reconstruction by half a unit cell]. Since the random shift proposed for the Ba/Si(111)-(3×2) surface was stated to be stable at room temperature,²⁰ it can hardly explain the formation of large (3×2) and $c(6 \times 2)$ domains by cooling the sample. In theoretical calculations performed for the Ba/Si(111)-(3×2) surface, the surface energies for T_4 and H_3 adsorption sites were reported to be comparable (the former adsorption site was reported to be only 0.01 eV/Ba lower than the latter adsorption site in Refs. 16 and 23, and 0.035 eV/Ba lower in Ref. 20). By assuming that the surface energies for Ca adsorptions on the T_4 and H_3 sites are close to those of Ba adsorption, the energy values reported in the theoretical studies^{16,20,23} suggest that Ca atoms can change its adsorption site from a T_4 site to its neighbor T_4 site via an H_3 adsorption site at room temperature, while they hardly move at 100 K. Therefore, we conclude that the basic structure of the so-called Ca/Si(111)-(3×2) surface has both the (3×2) and $c(6 \times 2)$ periodicities, and the ×2 streaks observed at 300 K result from thermally induced diffusion of the Ca atoms along the chain. Although the surface has these two different domains, we simply refer to it as Ca/Si(111)-(3×2) from here on.

FIG. 3. ARPES spectra of the Ca/Si(111)-(3×2) surface measured along the $[\bar{1}10]$ direction using (a) $h\nu=21.2$ eV and (b) $h\nu=17$ eV, and (c) along the $[11\bar{2}]$ direction using $h\nu=21.2$ eV. The spectra in the $[\bar{1}10]$ direction were obtained using the out-of-plane polarization geometry and the spectra in the $[11\bar{2}]$ direction were measured using the in-plane polarization geometry. (d) Surface Brillouin zones of the Si(111)-(1×1), (3×1), and (3×2) surfaces.

As shown in Fig. 2, the use of a vicinal 1.1° tilted substrate allowed us to obtain a predominantly single-domain Ca/Si(111)-(3×2) surface, instead of the three-domain (3×2) surface that is normally obtained using an on-axis substrate due to the threefold symmetry of the Si(111) substrate. That is, the observation of only weak $\times 3$ spots in the $[1\bar{2}1]$ and $[\bar{2}11]$ directions indicates that a single-domain surface with a quite high quality was obtained in the present study, and thus ARPES spectra can be analyzed without the ambiguity caused by the contributions from the two other (3×2) domains in the spectra. To obtain the fundamental electronic structure of the Ca/Si(111)-(3×2) surface by minimizing the effect of thermally induced diffusion, we have performed the ARPES measurements at 100 K. ARPES spectra of the Ca/Si(111)-(3×2) surface obtained at 100 K are shown in Fig. 3, together with the SBZ's of the Si(111)-(1×1), (3×1), and (3×2) surfaces [Fig. 3(d)]. (a) and (b) are the spectra measured along the $[\bar{1}10]$ direction using $h\nu=21.2$ eV and 17 eV, respectively, and (c) displays the spectra measured along the $[11\bar{2}]$ direction using $h\nu=21.2$ eV. The spectra in the $[11\bar{2}]$ direction were measured using the in-plane polarization geometry (the electric field of the pho-

tons is parallel to the photoelectron emission plane), and the spectra measured along the $[\bar{1}10]$ direction were obtained using the out-of-plane polarization geometry (the photoelectron emission plane is perpendicular to that of the in-plane polarization geometry). As indicated in Fig. 3(d), the $[\bar{1}10]$ direction corresponds to the $\bar{\Gamma}-\bar{A}-\bar{K}-\bar{C}(\bar{M})$ direction, and the $[11\bar{2}]$ direction corresponds to the $\bar{\Gamma}-\bar{C}$ direction. The symbols $\bar{M}$ and $\bar{K}$ are the symmetry points of the (1×1) SBZ, and the symbols $\bar{A}$ and $\bar{C}$ are the symmetry points of the (3×1) SBZ. The angle-resolved photoelectron spectra were recorded at every 1° from emission angles (θ_e) of 0° to 70° in the $[\bar{1}10]$ direction, and from $\theta_e=0^\circ$ to 15° in the $[11\bar{2}]$ direction. The Fermi level position (E_F), which is indicated by dashed lines, was determined by measuring the metallic Fermi edge of a Ta foil fixed on the sample holder. No density of states is observed at the Fermi level in Figs. 3(a)–3(c). This result agrees well with the previous valence band studies of the Ca/Si(111)-(3×2) surface^{8,18,19} in which the electronic structure of this surface was stated to be semiconducting.

Figure 4(a) displays the band dispersions of the Ca/

FIG. 4. (Color online) Band dispersion of the Ca/Si(111)-(3 $\times$ 2) surface measured (a) along the $[\bar{1}10]$ and $[11\bar{2}]$ directions using $h\nu=21.2$ eV and (b) along the $[\bar{1}10]$ direction using $h\nu=17$ eV. The bold dashed lines are the valence-band edge and edges of pockets taken from Ref. 24, and the thin dashed lines represent the symmetry points indicated at the top of each figure. The contrast represents the second derivatives of the original ARPES spectra shown in Fig. 3.

Si(111)-(3 $\times$ 2) surface along the $[\bar{1}10]$ and $[11\bar{2}]$ directions obtained using $h\nu=21.2$ eV, and (b) shows the dispersion along the $[\bar{1}10]$ direction obtained using $h\nu=17$ eV. The intensities of the spectral features are approximately represented by the contrast in Fig. 4, which represents the second derivatives of the original ARPES spectra. Here we note that the validity of the use of the second derivative of the spectra was confirmed by comparing the binding energies and contrast in Fig. 4 with the binding energies and intensities of the spectral features in Fig. 3 (dark in Fig. 4 corresponds to the highest intensity in the spectra). The bold dashed lines are the valence band edge and edges of pockets taken from Ref. 24, and the thin dashed lines represent the symmetry points of the (1 $\times$ 1) and (3 $\times$ 1) SBZ's indicated at the top of each

figure. The valence-band maximum (VBM) is estimated from the binding energy of the Si 2*p* core level using the relation between $E_{B(\text{VBM})}$, E_F , and $E_{B(\text{Si}2p_{3/2})}$ given in Ref. 25.

Six states, labeled S_1 – S_4 , Σ_1 , and Σ_2 are clearly observed in the gap and a pocket of the bulk band projection in Fig. 4. The S_1 state, which is clearly observed in Fig. 4(b), has an upward dispersion from the $\bar{\Gamma}$ point to the $\bar{A}$ point and a downward dispersion from the $\bar{A}$ point to the $\bar{K}$ point in the $[\bar{1}10]$ direction. Along the $[11\bar{2}]$ direction, S_1 has a downward dispersion from the $\bar{\Gamma}$ point to the $\bar{C}$ point and an upward dispersion from the $\bar{C}$ point to the $\bar{\Gamma}$ point of the second SBZ. The dispersion width of S_1 is approximately 1.1 eV in the $[\bar{1}10]$ direction and approximately 0.2 eV in the $[11\bar{2}]$ direction. Both the S_2 and S_3 states disperse downward from the $\bar{\Gamma}$ point to the $\bar{A}$ point and upward from the $\bar{A}$ point to the $\bar{C}$ point along the $[\bar{1}10]$ direction. In the $[11\bar{2}]$ direction, S_2 disperses upward from the $\bar{\Gamma}$ point to the $\bar{C}$ point and downward from the $\bar{C}$ point to the $\bar{\Gamma}$ point of the second SBZ, and S_3 hardly disperses. The dispersion widths of S_2 and S_3 are approximately 0.65 eV and 0.55 eV in the $[\bar{1}10]$ direction, and the dispersion width of S_2 is approximately 0.3 eV in the $[11\bar{2}]$ direction. The dispersion features of the S_1 – S_3 states indicate that these three surface states follow a (3 $\times$ 1) periodicity instead of the (3 $\times$ 2) periodicity observed in LEED (Fig. 2).

The S_4 state is observed only in a small $k_{||}$ region, and thus we cannot give its dispersion features. However, since surface states, whose binding energies are the same as that of S_4 , were observed for the Na,²⁶ K,²⁷ and Ag (Refs. 6 and 28) adsorbed Si(111)-(3 $\times$ 1) surfaces, we conclude that S_4 is a surface state which originates from orbitals of Si atoms that form the HCC structure. The Σ_1 and Σ_2 states, which were not observed in previous ARPES studies performed on metal atom adsorbed Si(111)-(3 $\times$ 1) (Refs. 6,26,27 and 29) and (3 $\times$ 2) (Refs. 7,15,18 and 19) surfaces at room temperature, disperse upward from the $\bar{A}$ point to the $\bar{C}$ point. Three origins can be considered for these two states, i.e., direct bulk transitions, folding of bulk states by umklapp processes, and surface states. However, the calculated binding energies of bulk transitions are much higher than those of Σ_1 and Σ_2 at the $\bar{M}$ point,³⁰ and the observation of these two states at the same binding energies using different photon energies is unexpected in the case of bulk transitions. Further, there are no structures around the $\bar{\Gamma}$ point that could explain Σ_1 and Σ_2 in terms of surface umklapp. Therefore, we conclude that Σ_1 and Σ_2 are surface states of the Ca/Si(111)-(3 $\times$ 2) surface which were not described in the literature. The fact that the Σ_1 and Σ_2 states appear at the edge of the bulk band gap and are clearly observed only in the band gap supports this conclusion. In addition to the six surface states, another state (the B_u state), which is not observed on the Si(111)-(7 $\times$ 7) surface, is shown in Fig. 4. Since it completely follows the $\times 3$ periodicity in the $[11\bar{2}]$ direction and can be reproduced by folding the B state, this B_u state should result from the

FIG. 5. Surface state dispersions of the Ca/Si(111)-(3×2) surface along the $\bar{\Gamma}$ - $\bar{C}$ and $\bar{\Gamma}$ - $\bar{A}$ - $\bar{K}$ - $\bar{C}$ ($\bar{M}$) directions. The filled circles represent the peak and shoulder positions of the ARPES spectra obtained using $h\nu=21.2$ eV, and the open ones are those obtained using $h\nu=17$ eV. Solid gray lines are the theoretical surface state dispersions derived from the calculation for the Li/Si(111)-(3×1) surface (Ref. 9).

folding of a bulk state by a reciprocal lattice vector of the high-quality (3×2) surface used in the present study. A state that has the same dispersion feature as B_u and which was assigned as originating from an umklapp process was also reported on the Ba/Si(111)-(3×2) surface.¹⁵

In order to discuss the surface electronic structure of the Ca/Si(111)-(3×2) surface in more detail, we compare the band dispersions of the five surface states observed in the bulk band gap (the S_1 - S_3 , Σ_1 , and Σ_2 states) with the dispersions of the surface states obtained theoretically for the Li/Si(111)-(3×1) surface.⁹ The filled circles in Fig. 5 represent the peak and shoulder positions of the ARPES spectra obtained using $h\nu=21.2$ eV, and the open ones are those obtained using $h\nu=17$ eV. The gray solid lines, which are labeled S_1^+ , S_2^+ , and S_2^- , are the dispersions of the surface states derived from the theoretical calculation. As shown in Fig. 5, the dispersion features of S_1 - S_3 agree well with those of S_1^+ , S_2^+ , and S_2^- , and the relative binding energies of S_1 - S_3 show good agreement with those of the calculated states at $k_{||}$ larger than $0.9 \text{ \AA}^{-1}$. At $k_{||}$ smaller than $0.9 \text{ \AA}^{-1}$, the relative binding energies of S_1 and S_2 show good agreement with those of the calculated states whereas the binding energy of S_3 is different from that of S_1^+ , e.g., the gap between S_1^+ and S_2^+ was estimated to be approximately 0.2 eV at the $\bar{\Gamma}$ point and the gap between S_2 and S_3 is obtained to be approximately 0.4 eV at the $\bar{\Gamma}$ point in the present study.

In Ref. 9, S_1^+ was stated to originate from a linear combination of ϕ_c and ϕ_d , $S_1^+ \sim \phi_c + \phi_d$, where ϕ_c and ϕ_d are the orbitals of the c and d Si atoms shown in Fig. 1(a). Both the c and d Si atoms have sp^2 -like character, and thus this statement indicates that the S_1^+ state mainly originates from the π bond between the c and d Si atoms. Further, the description $S_1^+ \sim \phi_c + \phi_d$ suggests that the adsorbate hardly affects the dispersion features of this surface state. The negligible correlation between the π -bond state and the adsorbate is confirmed by the fact that this state is observed in the same

binding energy range (1.5–2.5 eV) as similar dispersion in previous studies performed on monovalent^{6,26–29} and divalent^{7,15,18,19} atom induced Si(111)-(3×1) and (3×2) HCC surfaces. Therefore, since (1) the basic structure of the Ca/Si(111)-(3×2) surface is the same as the HCC structure of the Li/Si(111)-(3×1) surface,^{17–19} (2) the dispersion of S_3 shows good agreement with that of S_1^+ at $k_{||}$ larger than $0.9 \text{ \AA}^{-1}$, and (3) the S_3 state is observed in a binding energy range of 1.5–2.5 eV, we conclude that the origin of S_3 is the π -bond state between the C and D Si atoms displayed in Fig. 1(b). That is, S_3 is a linear combination of ϕ_C and ϕ_D ($S_3 \sim \phi_C + \phi_D$) where ϕ_C and ϕ_D are the orbitals of the C and D Si atoms, respectively. Concerning the difference between S_3 and S_1^+ at $k_{||}$ smaller than $0.9 \text{ \AA}^{-1}$, it can result either from a small modification of the HCC structure that might be caused by the adsorption of Ca atoms or from an overestimation of the dispersion width of S_1^+ in the theoretical calculation. However, we do not discuss this difference in detail since information about this state around the $\bar{\Gamma}$ point is missing in previous experimental studies performed on metal atom induced Si(111)-(3×1) surfaces, and because this small difference should not affect the conclusion about the origin of the S_3 state.

According to the theoretical calculation,⁹ S_2^+ and S_2^- were stated to originate from linear combinations of ϕ_a and ϕ_b ($S_2^\pm \sim \phi_a \pm \phi_b$), where ϕ_a and ϕ_b are the orbitals of the a and b Si atoms. Of these two calculated surface states, the S_2^- state was predicted to have a quite small photoemission cross section in the measurement using the in-plane geometry along the $[\bar{1}10]$ direction which results from the presence of an approximate mirror-plane symmetry of the HCC structure. On the other hand, the cross section of S_2^+ was reported not to have such dependence.⁹ In the present study, the S_1 state was hardly observed along the $[\bar{1}10]$ direction using the in-plane geometry (not shown in this paper) but clearly observed using the out-of-plane geometry as shown in Fig. 4, and the S_2 state was observed using both geometries. This result indicates that both the dispersion features and the photoemission cross section of S_1 and S_2 agree well with those of the S_2^+ and S_2^- states. The HCC structure with a 1/6 ML coverage leads, however, to a surface where some Si atoms have a different environment compared to the 1/3 ML HCC structure. It is therefore not possible to make a one-to-one comparison between our experimental data and the available calculations since all surface states are not accounted for by the 1/3 ML HCC model. As shown in Fig. 1, each b Si atom neighbors two metal atoms in a 1/3 ML coverage structure, while each B Si atom neighbors one metal atom in a 1/6 ML coverage structure, and there are two different kinds of Si atoms that correspond to the a Si atom. The A Si atom faces one metal atom and the A' Si atom does not face a metal atom. These differences indicate that, concerning the outermost Si atoms that face the channels, one has to consider three different orbitals (the ϕ_A , $\phi_{A'}$, and ϕ_B orbitals) to discuss the origins of surface states in the case of a 1/6 ML coverage HCC structure instead of the two (the ϕ_a and ϕ_b orbitals) considered for a 1/3 ML coverage structure.

To discuss the surface states related to the ϕ_A , $\phi_{A'}$, and ϕ_B orbitals, we assume that they originate from the linear combinations of the three orbitals as $(\phi_A \pm \phi_{A'}) \pm \phi_B$. By using this description, two more surface states should be observed on the Ca/Si(111)-(3×2) surface compared to the 1/3 ML AM adsorbed Si(111)-(3×1) surface. Since the HCC structure is reported to be stabilized by the donation of two electrons per (3×2) unit cell¹⁶ and the adsorbate coverage is 1/6 ML on the Si(111)-(3×2) surface, the interaction between Ca and Si atoms should be mainly ionic. This means that the perturbation caused by Ca atoms should be small, and thus that the difference between the symmetries of ϕ_A and $\phi_{A'}$ would be small. In this case, $\phi_{A'}$ can be replaced by ϕ_A when the phases of the two orbitals are the same, and the description $\phi_A + \phi_{A'}$ can be simplified to ϕ_A . According to the simplification, one can transform $(\phi_A + \phi_{A'}) \pm \phi_B$ into $\phi_A \pm \phi_B$, i.e., a description that is completely the same as that used for the origins of the S_2^+ and S_2^- states. Taking this result and the good agreement between S_1 and S_2^- and between S_2 and S_2^+ into account, we conclude that the origins of the S_1 and S_2 states are $\phi_A - \phi_B$ and $\phi_A + \phi_B$, respectively.

In contrast to the in-phase case, no simplification can be used when ϕ_A and $\phi_{A'}$ are out of phase, i.e., the description $(\phi_A - \phi_{A'}) \pm \phi_B$ cannot be simplified. This suggests that, although the dispersions of the two surface states described as $\phi_A \pm \phi_B$ follow a (3×1) periodicity since the description is the same as that used for surface states of an AM induced Si(111)-(3×1) surface, the two others expected by considering the presence of three different orbitals should follow a (3×2) periodicity. Concerning the Σ_1 and Σ_2 states, one notices that two possible origins can be considered. First, these states may be surface states originating from the HCC structure, e.g., the back bonds of the *A* and *B* Si atoms, that have not been discussed in the literature. Second, these states could be surface states that originate from the ×2 periodicity of the Ca induced HCC surface, i.e., surface states peculiar to the Ca/Si(111)-(3×2) surface. However, since the Σ_1 and Σ_2 states were not observed on monovalent atom induced Si(111)-(3×1) surfaces,^{6,26–29} the first alternative is inappropriate, and we conclude that these two states are surface states that originate from the difference between the 1/3 ML coverage and 1/6 ML coverage HCC structures. We therefore propose that the origins of the Σ_1 and Σ_2 states are $(\phi_A - \phi_{A'}) \pm \phi_B$.

Finally, we would like to discuss the dispersions of the surface states perpendicular to the chain direction (the $[11\bar{2}]$ direction). On a Ba/Si(111)-(3×2) surface,¹⁵ it was reported that S_1 has a slight upward dispersion and S_3 has a downward dispersion from the $\bar{\Gamma}$ point to the $\bar{C}$ point. These dispersions do not agree with those observed in the present study. Since S_2 and S_3 were reported to be degenerate at the $\bar{\Gamma}$ point in Ref. 15, the inconsistency between the previous

and present studies might originate from the lack of detailed information about the S_3 state around the $\bar{\Gamma}$ point in Ref. 15. Among the three surface states observed along the $[11\bar{2}]$ direction in the present study, the negligible dispersion of the S_3 state indicates that this state has a strong 1D character. Of the two other surface states, the dispersion width of S_2 is 1/6 of its dispersion width along the $[\bar{1}10]$ direction. This value suggests that the 1D electronic character of the S_2 state is weaker than that of S_3 . Regarding S_1 , its dispersion width along the $[11\bar{2}]$ direction, which is as large as half of its dispersion width along the $[\bar{1}10]$ direction, indicates the electronic character of this state to be quasi-1D. Taking the origins of S_1 and S_2 into account, these results suggest that the interaction between neighboring Ca chains is not negligible, and therefore supports the observation of the ×2 spots in LEED at 100 K.

IV. CONCLUSION

In conclusion, we have studied the electronic structure of the Ca/Si(111)-(3×2) surface along the $[\bar{1}10]$ and $[11\bar{2}]$ directions. Five states, none of which crosses the Fermi level, were observed in the bulk band gap and one state was observed in the bulk band pocket. Of the five states observed in the band gap, the dispersions of S_1 – S_3 follow a (3×1) periodicity instead of the clear (3×2) periodicity observed in LEED. Further, they show good agreement with the dispersions of the surface states obtained theoretically for monovalent atom adsorbed Si(111)-(3×1) surfaces in the $[\bar{1}10]$ direction. This indicates that S_1 – S_3 are surface states whose origins are the same as or quite similar to those of the Si(111)-(3×1) surfaces. The two other states observed in the band gap, the Σ_1 and Σ_2 states, were not reported in the literature. Taking the difference between a HCC structure with a 1/6 ML coverage and a HCC structure with a 1/3 ML coverage into account, we conclude that these two states are surface states peculiar to the Ca/Si(111)-(3×2) surface. The finite dispersion widths of S_1 and S_2 in the direction perpendicular to the chains ($[11\bar{2}]$) suggest that the electronic character is not completely 1D. This result indicates that the interaction between neighboring Ca chains is not negligible, and therefore supports the observation of the ×2 spots in LEED at 100 K.

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