

Atomic and electronic structures of metal induced Si(111)-(3×1) reconstructed surfaces

Kazuyuki Sakamoto*
Department of Physics, Graduate School of Science, Tohoku University, Sendai, 980-8578, Japan

R. I. G. Uhrberg
Department of Physics and Measurement Technology, Linköping University, 581 83 Linköping, Sweden

(Received 31 August 2004; Accepted 29 September 2004; Published 5 October 2004)

In this review, we present a series of photoemission studies performed on the so-called metal induced Si(111)-(3×1) surface, which is one of the most well known 1D structure formed on a Si(111) surface. Three different kinds of metals have been used as adsorbate, K, Ca, and Ag. On the K/Si(111)-(3×1) surface, five surface components were observed in the Si 2p core-level spectra. The energy shift and intensity of each surface component indicates that this surface has the honeycomb-chain-channel (HCC) structure with a K coverage of 1/3 ML. The extra spots observed in the LEED pattern of the so-called Ca/Si(111)-(3×1) surface suggest that this surface has a (3×2) periodicity instead of the (3×1) periodicity reported in the literature. By considering the energy shift and intensity of each Si 2p surface component, we conclude that the structure of the (3×2) phase is basically the same as that of the HCC model, but with a Ca coverage of 1/6 ML. Regarding the valence-band, five surface states, none of which crosses the Fermi level, were observed in the bulk band gap. The dispersion features of three of them agree well with those of monovalent atom adsorbed Si(111)-(3×1) surfaces along the chain direction. The two other states observed in the band gap have not been reported in the literature, and they are interpreted as surface states that are peculiar to the Ca/Si(111)-(3×2) surface due to the 1/6 ML coverage. Regarding the Ag/Si(111) surface, a new c(12×2) phase is observed in LEED after cooling the room temperature (6×1) phase to 70 K. In the Si 2p core-level spectra and in the valence band spectra, no significant difference is observed between the two surfaces. Further, the origins of the Si 2p surface components and the surface states of these surfaces are well explained using the HCC model. These results indicate that the basic structure of this Ag/Si(111) surface is quite similar with the HCC model but with a c(12×2) periodicity, and that the (6×1) structure results from thermal vibrations of the surface atoms. [DOI: 10.1380/ejssnt.2004.210]

Keywords: 1-D atomic chains; Photoelectron spectroscopy; LEED; Silicon; Surface structure; Surface states

I. INTRODUCTION

Semiconductor surfaces modified by the adsorption of metal atoms have been a topic of experimental investigation for the creation of nanoscale quantum structures with high perfection. Together with this technological importance, these nanoscale structures have been discussed in terms of various exotic physical phenomena, such as charge density wave and spin-charge separation [1–4]. Of the great number of metal induced surface reconstructions, the Si(111)-(3×1) surface is one of the most well known. This kind of Si(111)-(3×1) surface has been reported to be formed by various adsorbates, e.g., alkali metals (AM’s), alkaline-earth metals (AEM’s), rare-earth metals (Eu, Sm and Yb), and Ag with a coverage of 1/3 monolayer (ML). Although some of the adsorbates actually show different diffraction patterns (Ag shows a (6×1) pattern [5, 6], Ca [7], Eu and Yb [8] show a (3×2) pattern) all reconstructed surfaces are widely believed to have a quite similar structure based on the similarity of the low-energy electron diffraction (LEED) I-V curves [9, 10], scanning-tunneling-microscopy (STM) images [11–15], and surface core-level shift (SCLS) measurements [15–18].

The atomic geometry of the metal adsorbed Si(111)-(3×1) surface has been studied using a vast number of experimental and theoretical methods, and several structural models have been proposed so far [14, 19–23]. Figure 1 shows the two structural models proposed in the early studies; (a) the missing-top-layer (MTL) model (or the Seiwatz model) [19–21], and (b) the extended-Pandey-chain (EPC) model [16, 22]. The gray circles represent metal atoms, the green and yellow circles are Si atoms, and the bold dashed lines indicate the (3×1) unit cell. Both the MTL model and the EPC model consist of parallel π-bonded chains, which are formed by the green Si

![FIG. 1: Structural models proposed for the metal induced Si(111)-(3×1) reconstruction in the early studies; (a) the missing-top-layer model (or Seiwatz model) and (b) the extended-Pandey-chain model. Gray circles represent metal atoms, green circles are Si atoms that form π-bonded chains, and yellow circles are other Si atoms. The bold dashed lines indicate the (3×1) unit cell in each model.](image-url)
atoms in Fig. 1. These two models have been extensively debated as being the most plausible candidates of the atomic structure of the metal adsorbed Si(111)-(3×1). However, the Si atom densities of the reconstructed layers, which are 2/3 ML and 2 ML in the MTL and EPC models, respectively, do not fit the value of 4/3 ML that is obtained experimentally by STM [14].

In 1998, a model that is energetically more stable than the former ones was reported independently by several groups [24–26]. This model, called the honeycomb-chain-channel (HCC) model [24–26], is fully compatible with the SCLS results and the STM images. Further, the Si atom density of the reconstructed layer, which is 4/3 ML in the HCC model, is consistent with the value obtained experimentally [14]. In this model, the green Si atoms labeled “c” and “d” rehybridize from $sp^3$ into $sp^2$ and $p_z$, and form π bonds. Based on the HCC model, the electronic structures of the Na/ and Li/Si(111)-(3×1) surfaces were calculated by density-functional theory [26] and local-density approximation [24]. The good agreement between the experimental and calculated results supports the HCC model for the AM/Si(111)-(3×1) surfaces, and gives the following pictures for the origins of the surface states. Of the three surface states observed in the bulk band gap, one originates from a linear combination of $\phi_c$ and $\phi_d$, where $\phi_c$ and $\phi_d$ are the orbitals of the “c” and “d” Si atoms shown in Fig. 2. Since both the “c” and “d” Si atoms have a $sp^2$-like character, this statement indicates that one surface state mainly originates from the π-bond between the “c” and “d” Si atoms. Regarding the two other surface states, they are reported to originate from linear combinations of $\phi_a$ and $\phi_b$ ($\phi_a \pm \phi_b$), where $\phi_a$ and $\phi_b$ are the orbitals of the “a” and “b” Si atoms.

In this review, we present a series of our photoemission studies on the so-called metal induced Si(111)-(3×1) surface, i.e., the K/Si(111)-(3×1) surface, the Ca/Si(111)-(3×2) surface, and the Ag/Si(111)-(6×1) surface. All high-resolution photoemission measurements were performed at beamline 33 at the MAX-I synchrotron radiation facility in Lund, Sweden, using an angle-resolved photoelectron spectrometer.

**FIG. 3:** LEED pattern of the three domain K/Si(111)-(3×1) surface obtained with $E_p = 60$ eV at 100 K.

**II. HIGH-Resolution Si 2P Core-Level Study of the K/Si(111)-(3×1) Surface [27]**

Due to its simple electronic structure, the adsorption of AM, which has only a single $s$ electron interacting with the surface, is one of the prototype systems to study metal/semiconductor interfaces. Among the reconstructions of AM/Si(111) surfaces, the (3×1) structure, which is formed with a coverage of 1/3 ML, is observed for all AM’s [28]. Figure 3 shows the LEED pattern of the three domain K/Si(111)-(3×1) surface obtained with a primary electron energy ($E_p$) of 60 eV at 100 K. The sharp ×3 LEED spots, the low background, and the absence of any extra LEED spots indicate the high-quality of the K/Si(111)-(3×1) surface.

In Fig. 4, we show the Si 2$p$ core-level spectra of the K/Si(111)-(3×1) surface recorded at 100 K using $h\nu = 130$ eV (open circles are the experimental data). The spectrum in (a) was recorded with $\theta_e = 0^\circ$, and the spectrum in (b) with $30^\circ$ (different $\theta_e$ gives a difference in the surface sensitivity). The spectra in Fig. 4 look slightly different from those observed previously for the Si(111)-(3×1) surfaces formed using Li [17], Na [15, 16], and Cs [18]. That is, the flat area observed on the lower binding energy side of the main peak in (b) was not observed in the previous studies. This difference might come from the lower resolution of the experimental setups in the previous studies and/or from the use of a different alkali-metal species in our study. The presence of the flat part indicates that there are at least two surface components on the lower binding energy side of the main peak.

To identify the Si 2$p$ components that contribute to the spectral shape, and to obtain quantitative information on them, we have analyzed the spectra by a standard least-squares-fitting method using spin-orbit Voigt functions. The solid lines overlapping the data are the fitting curves. We used 608 meV for the spin-orbit splitting and a 80 meV full width at half maximum (FWHM) for the Lorentzian contribution for all components in the fitting procedure. The Gaussian widths of the bulk components (black components) are 210 meV (FWHM) in the two spectra, and those of the surface components are between 275 and 332 meV. A polynomial background was subtracted before the decomposition of each spectrum, and each component is indicated by different color. From the results of the fitting procedure, we realize that one bulk component and five surface components compose the Si 2$p$ spectra.
FIG. 4: Si 2p core-level spectrum of the K/Si(111)-(3×1) surface measured at 100 K using $h\nu = 130$ eV, and different $\theta_e$ that give a difference in the surface sensitivity. The spectrum in (a) was recorded with $\theta_e = 0^\circ$, and the spectrum in (b) with $30^\circ$. The open circles are the experimental data, and the solid lines overlapping the circles are the fitting results that are obtained using the components shown below each spectrum.

In order to discuss the origins of the surface components shown in Fig. 4, we first compare the present result with the previous Si 2p core-level studies performed for the AM’s induced Si(111)-(3×1) surfaces [15–18]. In these previous Si 2p core-level studies, only two surface components were observed. One component was shifted approximately -0.45 eV to the lower binding energy side, and the other one was shifted approximately +0.3 eV to the higher binding energy side. The shift to lower binding energy suggests a gain of electronic charge, and thus the surface component shifted to the lower binding energy side was assigned to Si atoms that face AM atoms. The component shifted to the higher binding energy side was assigned to top-layer Si atoms, i.e., the Si atoms labeled a-d in Fig. 2, and that S3-S5 might have contribution from Si atoms of the second and third layers. In the top-layer, two Si atoms face K atoms and two do not in the (3×1) unit cell of the HCC model [24–26].

As shown in Fig. 2, the “a” and “b” Si atoms have different K-Si arrangements, i.e., the “a” atoms face only one K atom, whereas the “b” atoms face two K atoms. This inequivalent arrangement was suggested to make a difference in the negative charge states of the “a” and “b” atoms in a theoretical calculation [26]. Therefore, we assign the S1 and S2 components to Si atoms that face K atoms though we are not able to determine which atom corresponds to which component.

The top-layer Si atoms that do not face K atoms, i.e., the atoms labeled “c” and “d” in Fig. 2, are suggested to rehybridize into $sp^2$ and $pz$ orbitals [24, 26] and form $\pi$ bonds as mentioned above. These $\pi$-bonded Si atoms are reported to be positively charged, and to have an energy shift of approximately +370 meV [26]. In the present study, the component that shows the closest energy shift is S3. However, the intensity dependence in emission angle suggests that its origin is not only the top-layer Si atoms. Taking into account that the Gaussian width of S3 was approximately 45 meV larger than the other components, we propose that S3 originates from the $\pi$-bonded Si atoms of the top-layer and some Si atoms of the second and third layers. For S4 and S5, although we are not able to point out their origins accurately, the emission angle dependent intensities of these components indicate their origins to be the second and third layer Si atoms that do not contribute to S3 and have slightly different charge states compared to the bulk Si atoms.

III. ATOMIC STRUCTURE AND SURFACE STATES OF THE Ca/Si(111)-(3×2) SURFACE [29, 30]

The electronic structures of the (3×1) surfaces formed by AM adsorption are expected to show semiconducting characters according to the even number of valence electrons in the unit cell. This expectation agrees well with the semiconducting electronic structures obtained experi-
mentally [13, 16, 17, 19]. In the case of AEM adsorption, experimental studies reported semiconducting characters for Ca [31], Mg [32], and Ba [33] adsorbed Si(111)-(3×1) surfaces. However, 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. Regarding the Ba adsorbed surface, this inconsistency was explained by the presence of a (3×2) periodicity, which was clearly observed using STM [34] but not in electron diffraction studies [33, 35], and from the estimated Ba coverage [34]. That is, a surface with a (3×2) periodicity and a Ba coverage of 1/6 ML (Fig. 5) lead to an even number of valence electrons in the unit cell, and thus explain well the semiconducting character of the so-called Ba/Si(111)-(3×1) surface. In contrast to the Ba case, the semiconducting characters of Ca [31] and Mg [32] adsorbed Si(111)-(3×1) surfaces were proposed to originate from strong electron correlations that might result from the 1D structure. This proposition was based on the assumption that the geometric structures of Ca and Mg induced Si(111)-(3×1) surfaces are completely the same as the HCC model, i.e., a surface with a (3×1) periodicity and an adsorbate coverage of 1/3 ML. However, so far there is no detailed study about the geometric structure of the Ca/Si(111)-(3×1) surface, and thus there is no evidence to support this proposition.

Concerning the electronic structure of the Ca/Si(111)-(3×1) surface, four studies have reported the surface band structure so far [31, 36–38]. 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 [31, 36], while three surface states were observed in the two others [37, 38]. Further, those studies do not provide a consistent picture of the surface state dispersions.

Figure 6 shows the LEED pattern of the so-called Ca/Si(111)-(3×1) surface obtained at 100 K using $E_p = 82$ eV. Together with the strong ×3 spots, some extra spots are clearly observed in the [112] direction. The extra spots correspond to the half-order spots of (3×2) and c(6×2) reconstructions, and thus the pattern in Fig. 6 indicates that the surface consists of large (3×2) and c(6×2) domains. Therefore, we conclude that the basic structure of the so-called Ca/Si(111)-(3×1) surface has both the (3×2) and c(6×2) periodicities. Although the surface has these two different periodicities, we simply refer to it as Ca/Si(111)-(3×2) from here on.

**A. Si 2p core-level study**

Quantitative information about the atomic structure, is obtained by analyzing the Si 2p spectra by a standard least-squares-fitting method using spin-orbit split Voigt functions. Figure 7 shows the results of the analysis for the Si 2p core-level spectrum of the Ca/Si(111)-(3×2) surface obtained with $\hbar\nu = 125$ eV and $\theta_e = 0^\circ$. The open circles are the experimental data, and the solid lines overlapping the data are the fitting curves. We used the same spin-orbit splitting and Lorentzian contribution for all components in the fitting procedure as those used for the K/Si(111)-(3×1) surface. The Gaussian widths of the bulk components are 225 meV (FWHM), and those of the surface components are between 268 and 312 meV. A polynomial background was subtracted before the decomposition of each spectrum, and each component is indicated by different color. From the result of the fitting procedure, we can conclude that the Ca/Si(111)-(3×2) surface has three surface components, a number which is larger than that reported previously for this surface [31].

Comparing the experimental results and calculations performed on a 1/3 ML Ca adsorbed Si(111)-(3×2) surface, the surface component observed on the lower binding energy side of the bulk component was assigned to originate from the Si atoms that face Ca atoms, i.e., the “a” and “b” Si atoms in Fig. 2, in the former Si 2p core-level study [31]. The surface component observed on the higher binding energy side of the bulk component was assigned to originate from the second layer Si atoms that are situated just below the Ca atoms [31]. However, the number of surface components is different from that observed in the present study. Further, a structural model with a
(3×1) periodicity and a Ca coverage of 1/3 ML, was used to attribute the origins of the surface components in that study, while the periodicity of the basic structure is actually (3×2) as shown in the present study and the accurate Ca coverage of this phase was undetermined. These mean that we cannot use the previous assignments to identify to origins of the surface components shown in Fig. 7.

In the case of AM’s adsorbed Si(111)-(3×1) surfaces [26, 27], the two surface components, whose binding energies are lower than that of the bulk component, were attributed to originate from the surface Si atoms that face the adsorbate as mentioned in the previous section. In a theoretical calculation performed on the Na/Si(111)-(3×1) surface [26], the surface component with the lowest binding energy is assigned to originate from the “h” Si atoms, and the component with the second lowest binding energy is expected to result from the “a” atoms. Taking into account that different arrangements produce different surface components for the AM adsorbed Si(111)-(3×1) surfaces, and that there are also two different Ca-Si arrangements in both the (3×1) and (3×2) phases as shown in Figs. 2 and 5, we regard the S1 and S2 components to originate from Si atoms that face Ca atoms.

The intensity ratio of the surface components gives information about the number of corresponding Si atoms in the unit cell, which makes it possible to obtain more accurate information about the geometric structure of the Ca/Si(111)-(3×2) surface and to make more precise assignments of the origins of S1 and S2. In Fig. 7, the intensity ratio of S1 and S2 was approximately 2:1. Even by modifying the Ca adsorption sites and by forming a (3×2) periodicity, a ratio of 2:1 cannot be achieved using a Ca coverage of 1/3 ML, i.e., a coverage proposed in the early studies [7, 31]. Since the accurate coverage of Ca was not measured in the early studies, and the 1/3 ML coverage was only based on the assumption that the coverage of Ca is the same as that of the AM/Si(111)-(3×1) surfaces, we have investigated the adsorbate coverage of the Ca/Si(111)-(3×2) surface by the Ca deposition time and the Ca 3p core-level spectra. The deposition time to obtain the Ca/Si(111)-(3×2) surface was 0.35 of the time to obtain a Ca/Si(111)-(2×1) surface, and the intensity ratio of the Ca 3p core-level spectra, normalized using the background intensities that are proportional to the photon flux, was 0.31:1 for the (3×2) and (2×1) surfaces. Based on these ratios and on the 0.5 ML Ca coverage of the (2×1) surface [7, 31], we conclude that the Ca/Si(111)-(3×2) surface has the HCC structure with a Ca coverage of 1/6 ML. This conclusion indicates that the geometric structure of the Ca/Si(111)-(3×2) surface is the same as that of the Ba/Si(111)-(3×2) surface, and therefore supports the proposition [34] that the geometric structures of all AEM’s adsorbed Si(111)-(3×2) surfaces are universal. By using the 1/6 ML model, we consider the origins of S1 and S2 shown in Fig. 7. As shown in Fig. 5, the number ratio of the “A” and “B” Si atoms is 2:1 in the unit cell. Since this ratio fits with the ratio of S1 and S2, we conclude that the origins of S1 and S2 are the “A” and “B” Si atoms, respectively.

The FWHM of S3 is larger than the FWHM’s of S1 and S2, and a larger FWHM suggests the possibility of more than one origin. Thus we propose that S3 originates from the “C”, “D”, and Si atoms situated below Ca atoms as well as the K/Si(111)-(3×1) surface. (The surface component produced by the “A’” atoms is discussed in Ref. 29.)

**B. Angle-resolved photoemission study**

Figure 8(a) displays the band dispersions of the Ca/Si(111)-(3×2) surface measured (a) along the [110] and [112] directions using $h\nu$ = 21.2 eV and (b) along the [110] direction using $h\nu$ = 17 eV. The bold dashed lines are the valence band edge and edges of pockets taken from Ref. 39, and the thin dashed lines represent the symmetry points indicated at the top of each figure.

The intensity ratio of the surface components gives information about the number of corresponding Si atoms in the unit cell, which makes it possible to obtain more accurate information about the geometric structure of the Ca/Si(111)-(3×2) surface and to make more precise assignments of the origins of S1 and S2. In Fig. 7, the intensity ratio of S1 and S2 was approximately 2:1. Even by modifying the Ca adsorption sites and by forming a (3×2) periodicity, a ratio of 2:1 cannot be achieved using a Ca coverage of 1/3 ML, i.e., a coverage proposed in the early studies [7, 31]. Since the accurate coverage of Ca was not measured in the early studies, and the 1/3 ML coverage was only based on the assumption that the coverage of Ca is the same as that of the AM/Si(111)-(3×1) surfaces, we have investigated the adsorbate coverage of the Ca/Si(111)-(3×2) surface by the Ca deposition time and the Ca 3p core-level spectra. The deposition time to obtain the Ca/Si(111)-(3×2) surface was 0.35 of the time to obtain a Ca/Si(111)-(2×1) surface, and the intensity ratio of the Ca 3p core-level spectra, normalized using the background intensities that are proportional to the photon flux, was 0.31:1 for the (3×2) and (2×1) surfaces. Based on these ratios and on the 0.5 ML Ca coverage of the (2×1) surface [7, 31], we conclude that the Ca/Si(111)-(3×2) surface has the HCC structure with a Ca coverage of 1/6 ML. This conclusion indicates that the geometric structure of the Ca/Si(111)-(3×2) surface is the same as that of the Ba/Si(111)-(3×2) surface, and therefore supports the proposition [34] that the geometric structures of all AEM’s adsorbed Si(111)-(3×2) surfaces are universal. By using the 1/6 ML model, we consider the origins of S1 and S2 shown in Fig. 7. As shown in Fig. 5, the number ratio of the “A” and “B” Si atoms is 2:1 in the unit cell. Since this ratio fits with the ratio of S1 and S2, we conclude that the origins of S1 and S2 are the “A” and “B” Si atoms, respectively.

The FWHM of S3 is larger than the FWHM’s of S1 and S2, and a larger FWHM suggests the possibility of more than one origin. Thus we propose that S3 originates from the “C”, “D”, and Si atoms situated below Ca atoms as well as the K/Si(111)-(3×1) surface. (The surface component produced by the “A’” atoms is discussed in Ref. 29.)
FIG. 9: Surface state dispersions of the Ca/Si(111)-(3×2) surface along the Γ-C and Γ-A-K-C(M) directions. The filled red are obtained using \( h\nu = 21.2 \) eV, and the open blue ones are 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. 24].

The \( S_1 \) state, which is clearly observed in Fig. 8(b), has an upward dispersion from the \( \Gamma \) point to the \( A \) point and a downward dispersion from the \( A \) point to the \( K \) point in the [110] direction. Along the [112] direction, \( S_1 \) has a downward dispersion from the \( \Gamma \) point to the \( C \) point and an upward dispersion from the \( C \) point to the \( \Gamma \) point of the second SBZ. Both the \( S_2 \) and \( S_3 \) states disperse downward from the \( \Gamma \) point to the \( A \) point and upward from the \( A \) point to the \( C \) point along the [110] direction. In the [112] direction, \( S_2 \) disperses upward from the \( \Gamma \) point to the \( C \) point and downward from the \( C \) point to the \( \Gamma \) point of the second SBZ, and \( S_3 \) hardly disperses. The dispersion features of the \( S_1 \)-\( S_3 \) states indicate that these three surface states follow a \((3\times1)\) periodicity instead of the \((3\times2)\) periodicity observed in LEED (Fig. 6).

The \( \Sigma_1 \) and \( \Sigma_2 \) states, which are not observed in the former ARPES studies performed on metal atoms adsorbed Si(111)-(3\times1) [17, 19, 41] and (3\times2) [32, 33, 36, 37] surfaces at room temperature, disperse upward from the \( \Lambda \) point to the \( C \) 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 \( \Sigma_1 \) and \( \Sigma_2 \) at the \( M \) point [42], 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 is no structure around the \( \Gamma \) point that could explain \( \Sigma_1 \) and \( \Sigma_2 \) in terms of surface umklapp. Therefore, we conclude that \( \Sigma_1 \) and \( \Sigma_2 \) are surface states of the Ca/Si(111)-(3\times2) surface which were not observed in the literature. The fact that the \( \Sigma_1 \) and \( \Sigma_2 \) states appear at the edge of the bulk band gap and are clearly observed only in the band gap supports this conclusion.

In order to discuss the surface electronic structure of the Ca/Si(111)-(3\times2) surface in more detail, we compare the band dispersions of the five surface states observed in the bulk band gap (the \( S_1 \)-\( S_3 \), \( \Sigma_1 \), and \( \Sigma_2 \) states) with the dispersions of the surface states obtained theoretically for the Li/Si(111)-(3\times1) surface [24]. The filled red circles in Fig. 9 are the results obtained using \( h\nu = 21.2 \) eV, and the open blue ones are those obtained using \( h\nu = 17 \) eV. The gray solid lines, which are labeled \( S_1^+ \), \( S_3^+ \), and \( S_2^+ \), are the dispersions of the surface states derived from the theoretical calculation. As shown in Fig. 9, the dispersion features of \( S_1 \)-\( S_3 \) agree well with those of \( S_1^+ \), \( S_3^+ \), and \( S_2^+ \), and the relative binding energies of \( S_1 \) and \( S_2 \) show good agreement with those of the calculated states at \( k_{\perp} \) larger than 0.9 Å\(^{-1}\). At \( k_{\perp} \) smaller than 0.9 Å\(^{-1}\), 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 \( S_3^+ \), e.g., the gap between \( S_1^+ \) and \( S_2^+ \) was estimated to be less than 0.2 eV at the \( \Gamma \) point and the gap between \( S_2 \) and \( S_3 \) is obtained to be approximately 0.4 eV at the \( \Gamma \) point in the present study.

In Ref. 24, \( S_1^+ \) was stated as \( S_1^+ \sim \phi_c + \phi_d \), i.e., the \( \pi \)-bond between the “c” and “d” Si atoms. The description \( S_1^+ \sim \phi_c + \phi_d \) suggests that the adsorbate hardly affects the dispersion feature of this surface state. The negligible correlation between the \( \pi \)-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) with similar dispersion in the former studies performed on monovalent [17, 19, 41] and divalent atoms [32, 33, 36, 37] induced Si(111)-(3\times1) and (3\times2) HCC surfaces. Therefore, since (1) the basic structure of the Ca/Si(111)-(3\times2) surface is the same as the HCC structure of the Li/Si(111)-(3\times1) surface [29, 36, 37], (2) the dispersion of \( S_3 \) shows good agreement with that of \( S_3^+ \) at \( k_{\perp} \) larger than 0.9 Å\(^{-1}\), 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 \( \pi \)-bond state between the “c” and “d” Si atoms displayed in Fig. 5 (\( S_3 \sim \phi_c + \phi_D \), where \( \phi_C \) and \( \phi_D \) are the orbitals of the “c” and “d” Si atoms, respectively). Concerning the difference between \( S_3 \) and \( S_3^+ \) at \( k_{\perp} \) smaller than 0.9 Å\(^{-1}\), it can result from either 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 \( S_3^+ \) in the theoretical calculation.

According to the theoretical calculation [24], \( S_3^+ \) and \( S_2^+ \) were stated as \( S_2^+ \sim \phi_c \pm \phi_d \). Of these two calculated surface states, the \( S_3^+ \) state was predicted to have a quite small photoemission cross section in the measurement using the in-plane geometry along the [110] direction that results from the presence of an approximate mirror-plane symmetry of the HCC structure. On the other hand, the cross section of \( S_3^+ \) was reported not to have such dependence [24]. In the present study, the \( S_1 \) state was hardly observed along the [110] direction using the in-plane geometry but clearly observed using the out-of-plane geometry as shown in Fig. 8, 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 \( S_3^+ \) states. The HCC structure with a 1/6 ML coverage leads, however, to a surface where some Si atoms have a different symmetry of the HCC structure. On the other hand, the HCC structure with a 1/3 ML coverage leads, how-
kinds of Si atoms that correspond to the “a” Si atom in the HCC structure with a 1/6 ML coverage. 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 \( \phi_A, \phi_A’, \) and \( \phi_B \) orbitals) to discuss the origins of surface states in the case of a 1/6 ML coverage HCC structure instead of the two (the \( \phi_a \) and \( \phi_b \) orbitals) considered for a 1/3 ML coverage structure.

To discuss the surface states related to the \( \phi_A, \phi_A’, \) and \( \phi_B \) orbitals, we assume that they originate from the linear combinations of the three orbitals as \( \phi_A \equiv \phi_A \pm \phi_A’ \pm \phi_B \). 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. On the Ca/Si(111)-(2×1) surface, the interaction between Ca and Si atoms is reported to be mainly ionic [38, 43]. This means that the perturbation caused by Ca atoms should be small, and thus that the difference between the symmetries of \( \phi_A \) and \( \phi_A’ \) would be small. In this case, \( \phi_A’ \) can be replaced by \( \phi_A \) when the phases of the two orbitals are the same and the description \( \phi_A + \phi_A’ \) can be simplified as \( \phi_A \). 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 \( S^+ \) and \( S^- \) states. Taking this result and the good agreements between \( S_1 \) and \( S_2 \) and those 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. Further, this result supports the proposition that the HCC structure is stabilized by the donation of two electrons per \( (3\times2) \) unit cell [34].

In contrast to the in-phase case, no simplification can be used when \( \phi_A \) and \( \phi_A' \) are out-of-phase, i.e., the description \( \phi_A \equiv \phi_A' \) cannot be simplified. This suggests that although the dispersions of the two surface states described as \( \phi_A \equiv \phi_B \) follow a \( (3\times1) \) 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 \( (3\times2) \) periodicity. Concerning the \( S_1 \) and \( S_2 \) states, one notices that two possible origins can be considered. First, these states may be the surface states originating from the HCC structure, e.g., the backbonds 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 \( x \) periodicity of the Ca induced HCC structure, i.e., they are surface states peculiar to the Ca/Si(111)-(3×2) surface. However, since the \( S_1 \) and \( S_2 \) states were not observed on monovalent atom induced Si(111)-(3×1) surfaces [17, 19, 41], 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 \( S_1 \) and \( S_2 \) states are \( \phi_A - \phi_A' \equiv \phi_B \).

In the former studies, it was reported that the interaction between neighboring AEM chains is negligible and the AEM induced Si(111)-(3×1) surfaces have 1D electronic character [36, 44]. However, the observation of \( x \) spots in Fig.6 indicates that the interaction between neighboring Ca chains cannot be neglected (a negligible interaction produces \( x \) streaks and not \( x \) spots). Since there was no detailed study about the electronic structure perpendicular to the AEM chains so far, we would like to mention about the dispersions of the surface states perpendicular to the chain direction (the [\( \overline{112} \]) direction) at the end of this section. On a Ba/Si(111)-(3×2) surface [33], it was reported that \( S_1 \) has a slight upward dispersion and \( S_3 \) has a downward dispersion from the \( \Gamma \) point to the \( C \) 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 \( \Gamma \) point in Ref. 33, the inconsistency between the former and present studies might originate from the lack of detailed information of the \( S_2 \) state around the \( \Gamma \) point in Ref. 33. Among the three surface states observed along the [\( \overline{112} \)] 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 \( S_1 \) is 1/6 of its dispersion width along the [\( \overline{110} \)] direction. This value suggests that the 1D electronic character of the \( S_1 \) state is weaker than that of \( S_2 \). Regarding \( S_2 \), its dispersion width along the [\( \overline{112} \)] direction, which is as large as half of its dispersion width along the [\( \overline{110} \)] direction, indicates the electronic character of this state to be quasi-1D.

**IV. BASIC STRUCTURE OF THE Ag/Si(111)-(6×1) SURFACE [45]**

The structure of the Ag/Si(111)-(6×1) surface is reported to originate from a slight displacement of the surface atoms of the \( (3\times1) \) structure [6]. This report is based on the observation of the \( (3\times1) \leftrightarrow (6\times1) \) transition at a temperature of approximately 500 K [5, 6]. Figure 10 shows the structural model proposed for the Ag/Si(111)-(6×1) surface [24]. Driven by the formation of weak Ag-Si bond, which favors twofold coordination of the Ag atom, the Ag atom occupies an asymmetric location with respect to the [\( \overline{110} \)] direction. That is, the adsorption sites of Ag atoms (gray circles) are slightly shifted from the \( T_4 \) site (light gray circles), i.e., the adsorption site of AM...
on a Si(111)-(3×1) surface, as shown in Fig. 10. Using STM, both (3×1) [11, 12, 46–49] and (6×1) [14, 47–49] structures are observed at 300 K. Taking into account the observation of a tip induced (3×1) → (6×1) transition [47, 48], the (6×1) structure is suggested to be the stable phase, and the (3×1) structure a metastable one. This idea is supported by theoretical calculations [24, 50], in which the (6×1) phase is reported to have a slightly lower energy than the (3×1) phase. Despite these previous reports, the origin of the (3×1) ↔ (6×1) phase transition is not determined yet, and no accurate structural model has been proposed for the Ag/Si(111)-(6×1) surface up to now. Furthermore, since the adsorption of a different species on the same substrate structure might show a difference in the electronic structure, it is very exciting to study the electronic structures of Si(111)-(3×1) surfaces formed by metal atoms besides alkali and alkaline-earth metals.

A. LEED study

Figure 11(a) shows the LEED pattern of a three-domain Ag/Si(111)-(6×1) surface, obtained with \( E_p = 100 \) eV at 300 K. The 6 spots observed in Fig. 11 did not show up immediately after annealing the sample at 850 K, i.e., the annealing temperature to obtain an entirely uniform (6×1) surface. Instead they appear upon cooling the sample close to room temperature. This result agrees well with the previous studies [5, 6], in which the (3×1) → (6×1) phase transition is reported to occur near 500 K. Further, the absence of odd-order reflections in Fig. 11, which indicates the presence of a glide plane symmetry in the [112] direction, agrees well with the proposed structural model (Fig. 10). Since the surface has both stable (6×1) and metastable (3×1) phases at 300 K [47, 48, 50], we cooled down the sample to a lower temperature to obtain a more stable surface. Figure 11(b) shows the LEED pattern obtained with \( E_p = 58 \) eV at 70 K. In this LEED pattern, we clearly observe some extra spots that are not present at 300 K. Comparing the LEED pattern shown in Fig. 11(b) with the schematic pattern of Si(111)-(12×2) (Fig. 11(c)) we conclude that the surface structure has transformed to a c(12×2) structure at 70 K. Here we notice that the c(12×2) LEED pattern was also observed at 100 K.

B. Si 2p core-level study

In order to understand the origin of the (6×1) → c(12×2) phase transition, we have measured the Si 2p core-level at 300 and 100 K. Figure 12 shows the Si 2p core-level spectra of the Ag/Si(111)-(6×1) and c(12×2) surfaces obtained at \( h\nu = 130 \) eV. \( \theta_p \) is 0° in (a) and (b), and 60° in (c). The open circles are the experimental data, and the solid lines overlaying the data are the fitting curves. A 608 meV spin-orbit splitting and a 80 meV FWHM for the Lorentzian contribution were used for all components in the fitting procedure. The Gaussian widths of the bulk components (black components) are 217 and 212 meV (FWHM) for the (6×1) and c(12×2) surface, respectively, and those of the surface components were between 225 and 245 meV. A polynomial background was subtracted before the decomposition of each spectrum, and each component is indicated by different color. From the result of the fitting procedure, we can conclude that both the Ag/Si(111)-(6×1) and c(12×2) surfaces have three surface components that agree well in the energy shifts.

In the Si 2p core-level spectrum of the Ag/Si(111)-(√3×√3) surface [51], the surface component of Si atoms bonded directly to Ag atoms shows a shift of 250 meV to the higher binding energy side of the bulk component. Comparing the density of Ag and the number of surrounding Si atoms of the Ag/Si(111)-(√3×√3) surface [52] with that of the HCC model [24–26], the charge transfer to Ag from the surrounding Si atoms should be smaller on the Ag/Si(111)-(6×1) and/or Ag/Si(111)-c(12×2) surfaces. Since a smaller charge transfer leads to a smaller energy shift for the surface component, we assign the S1 component to Si atoms bonded directly to the Ag atoms. In order to make an assignment of the S2 and S3 components, we compare the Si 2p spectra obtained at different emission angles, i.e., Figs. 12(b) and (c). The intensities of the S1 and S2 components increase at the higher emission angle. On the other hand, the intensity of the S3 component hardly changes. This result suggests that the S1 and S2 components originate from the top-layer Si atoms and that S3 might correspond to second layer Si atoms. Further, comparing the intensity ratio of the S1 and S2 components, the number of Si atoms that contributes to S1 and S2 should be the same for the HCC model. Since two Si atoms of the top-layer are bonded directly to Ag and two are not in the HCC model [24–26], we assign S2 to the Si atoms that form π bonds. The energy shift of these π-bonded Si atoms is reported to be approximately +370 meV by a theoretical calculation [26], which supports our assignment of the S2 component.

At the end of this subsection, we would like to discuss the differences between the origins of the Si 2p components of the Ag induced HCC structure and those of the K and Ca induced ones. In the case of K and Ca induced HCC structures, Si atoms that face the adsorbates produce two Si 2p components, while only one component is produced from those atoms on the Ag induced HCC surface. Further, although the S2 component is assigned to the Si atoms that form π bonds in the case of Ag adsorbed surface, the corresponding components are assigned to originate from both the π-bonded Si atoms and the Si atoms situated just below the adsorbates in the case of K and Ca adsorbed surfaces. As shown in Fig. 10, the adsorption sites of Ag atoms are slightly shifted from the T4 site, and all Si atoms that face Ag atoms have equivalent Ag-Si arrangements. Since an inequivalent adsorbate-Si arrangement was suggested to make a difference in the negative charge states of the Si atoms and thus to produce two Si 2p components [26], the equivalent Ag-Si arrangement should produce only one Si 2p component. Moreover, the shift of Ag atoms might change the charge states of the Si atoms situated below them. These mean that the differences in the origins of the Si 2p components are well explained by the slightly different adsorption site of Ag atoms, and therefore support the structural model shown in Fig. 10.
FIG. 11: LEED pattern of the three domain Ag/Si(111)-(6×1) surface obtained with $E_p = 109$ eV at 300 K (a). The LEED pattern obtained with $E_p = 58$ eV at 70 K is displayed in (b). (c) shows the schematic LEED pattern of a three domain Si(111)-c(12×2) surface.

FIG. 12: Si 2p core-level spectra of the Ag/Si(111)-(6×1) surface measured at 300 K in (a), and the spectra of the Ag/Si(111)-c(12×2) surface measured at 100 K in (b) and (c). The three spectra were recorded with $h\nu = 130$ eV at $\theta_e = 0^\circ$ for (a) and (b), and 60° for (c). The open circles are the experimental data, and the solid lines overlapping the circles are the fitting results that are obtained using the components shown below each spectrum.

C. Valence-band study

Figure 13 displays the band maps along the [110] (Γ → K → M) and [112] (Γ → M) directions, respectively obtained from angle-resolved photoelectron spectra (the symbols Γ, M, and K are the symmetry points of the (1×1) SBZ). The open red circles represent the peak and shoulder positions observed in the valence band photoelectron spectra of the Ag/Si(111)-(6×1) surface, and the filled blue ones are those of the Ag/Si(111)-c(12×2) surface. The shaded area is the bulk band projection taken from Ref.39. The valence band maximum (VBM) is estimated from the binding energy of the Si 2p core level using the relation among $E_{B(VBM)}$, $E_F$, and $E_{B(Si2p3/2)}$ given in Ref.40.

Five states, labeled $S_1$-$S_5$, are clearly observed in the band gap and pockets of the bulk band projection. The binding energies of these states are approximately 1.1, 1.6, 2.1, 4.2, and 4.6 eV. Comparing their dispersions with those of the surface states observed previously for the AM and AEM adsorbed Si(111)-(3×1) and (3×2) surfaces [17, 19, 32, 41], we realize that the dispersions of the $S_1$-$S_5$ states are quite small. The dispersion widths of the two surface states with smallest binding energies ($S_1$ and $S_2$) are less than 0.2 eV for the Ag/Si(111)-(6×1) and c(12×2) surfaces, while values between 0.4 and 0.7 eV are found for AM and AEM adsorbed Si(111)-(3×1) and (3×2) surfaces [17, 19, 32, 41]. In the Na and K adsorbed Si(111)-(3×1) studies [19, 41], in which three equivalent (3×1) domains were also present, the large dispersion made it difficult to obtain the real number of surface states. That is, because one ARPES spectrum contains information of surface states at two different wave vectors and the large dispersion should produce a difference in binding energy of a state at different wave vectors, the number of the observed surface bands was larger than the real one. In the present study, though the measurements were also done along two directions of the SBZ simultaneously, the negligible dispersions help us to obtain the real number of surface states, as well as the band structures. Hence, we conclude that both the Ag/Si(111)-(6×1) and c(12×2) surfaces have five surface states with negligible dispersion that are located in the band gap and pockets of the bulk band projection. Moreover, no Fermi level crossing is observed on either the Ag/Si(111)-(6×1) or the Ag/Si(111)-c(12×2) surface. This result suggests a completely semi-conducting character of the two surfaces, and shows good agreement with the STS study [47, 48] in which a gap is observed for the Ag/Si(111)-(6×1) surface. Further, the binding energy of the $S_1$ state agrees well with the energy of a state observed at approximately 1 eV in this STS study.

Among the surface states observed experimentally on AM and AEM adsorbed Si(111)-(3×1) and (3×2) surfaces
FIG. 13: Band dispersion of the Ag/Si(111)-(6×1) and c(12×2) surfaces measured along the [1 \bar{1} 0] direction in (a), and [11\bar{2}] direction in (b). The open red circles represent the peak and shoulder positions observed in the valence band photoelectron spectra of the Ag/Si(111)-(6×1) surface, and the filled blue ones are those of the Ag/Si(111)-c(12×2) surface. The three different sizes of the circles have been used to indicate the intensity of the peaks and shoulders in the valence band photoelectron spectra. The shaded areas are the bulk band projection.

[17, 19, 32, 41], the origins of the three with the smallest binding energies are explained by theoretical calculations using the HCC model [24, 26]. The two states with lower binding energies are attributed to the bonding states between the adsorbates and the surface Si atoms, and the remaining one is assigned to the π-bond state formed by two Si atoms that are contained in the honeycomb. Since the structure of the Ag/Si(111)-c(12×2) surface is basically the same as that of the HCC model [24–26], but with a slight displacement of Ag and/or top-layer Si atoms to form a larger unit cell, the observation of surface states with the same origins as those on AM and AEM adsorbed Si(111)-(3×1) and (3×2) surfaces is expected. Since the π-bond state is located at approximately $E_B = 2$ eV on Na [41] and K [19] adsorbed Si(111)-(3×1) surfaces, and on Ca [30] and Ba [33] adsorbed Si(111)-(3×2) surfaces, the binding energy of this state is hardly affected by the adsorbate. Therefore, the same binding energy of the $S_3$ state, at 2.1 eV, suggests its origin to be the π-bond state. On AM and AEM adsorbed Si(111)-(3×1) and (3×2) surfaces, all surface states, which originate from the surface Si atoms that face the adsorbates have binding energies lower than 2 eV. Hence, we conclude that the origins of $S_1$ and $S_2$ are the Ag-Si bond. As we mentioned above, the structures of Ag/Si(111)-(6×1) and c(12×2) surfaces should be slightly different from the HCC model. This difference might result in a larger number of adsorbate bonding configurations compared to the HCC model, and thus a larger number of surface states on the Ag/Si(111)-(6×1) and c(12×2) surfaces. However, assuming that the displacement of surface atoms is too small to give large shifts in the binding energies of the surface states, it is reasonable to observe only two Ag-Si bonding states due to the finite experimental resolution.

D. Discussion

From the result of the Si 2p fitting procedure, we can conclude that both the Ag/Si(111)-(6×1) and c(12×2) surfaces have three surface components that agree well in the energy shifts. Such results for Si 2p core-level spectra from different surface structures, are also observed on the clean Si(001) surface [53]. That is, the room temperature Si(001)-(2×1) and low temperature c(4×2) phases show very similar Si 2p spectra and they have surface components with the same energy shifts [53]. In this case, the similarity of the Si 2p core-level spectra indicates that the local surface structure is the same for the two phases, and that the room temperature (2×1) phase results from the dynamical flipping of the asymmetric dimers [54] at a high frequency. Since the translational vectors of the c(12×2) unit cell are twice as long compared to the (6×1) reconstructed structure, there should be an alternate displacement of Ag atoms and/or the site of the top-layer Si atoms along both translational vectors. The observation of only the (6×1) pattern at a higher temperature can be explained by a disorder in the atomic displacements due to thermal vibrations in similarity with the clean Si(001) surface.

Regarding the binding energy and dispersion of the sur-
face states, no obvious difference is observed between the Ag/Si(111)-(6×1) surface and the Ag/Si(111)-(12×2) surface. Such result for surface states of different surface structures, is also observed on the clean Si(001) surface [55]. That is, the surface states of the room temperature Si(001)-(2×1) phase and those of the low temperature c(4×2) phase have quite similar binding energies and dispersions. In this case, the similarity of the surface states results from the fact that the room temperature (2×1) phase is due to thermally induced disorder of surface atoms and the local structures of the two surfaces are the same. Therefore, we conclude that the Ag/Si(111)-(12×2) surface is the basic structure, and the appearance of a (6×1) structure is a result of thermally induced disorder that hardly affects the electronic structure. This conclusion agrees well with the Si 2p core-level study that shows no significant difference between the (6×1) and c(12×2) surfaces. (Here we notice that the accurate structure of the Ag/Si(111)-(12×2) surface cannot be obtained using LEED and photoemission only, and further studies using other method, e.g., STM or photoelectron diffraction, are expected.)

To support this picture, we observed the LEED pattern of a surface where the (6×1) and (√3×√3) phases coexist at 300 K. Figure 14 shows the LEED pattern of the mixed Ag/Si(111)-(6×1) and (√3×√3) surface obtained with Eₚ = 75 eV at 300 K. Besides the spots from the (6×1) and (√3×√3) structures, weak ×2 streaks reveal the presence of the c(12×2) structure with frequent phase mismatching. The phase mismatching of the c(12×2) structure can be explained by pinning at the domain boundaries, and it supports the idea that thermally induced disorder in the atomic displacements causes the c(12×2) → (6×1) conversion.

V. CONCLUSION

We have presented a series of photoemission studies performed on the so-called metal induced Si(111)-(3×1) surface. In the Si 2p core-level spectra of the K/Si(111)-(3×1) surface, five surface components were observed. By considering the energy shift and intensity of each surface component, we have investigated the origins of the surface components. This result supports that this surface has the HCC structure with a K coverage of 1/3 ML. Using LEED, we observed a (3×2) periodicity for the so-called Ca/Si(111)-(3×1) surface. By considering the energy shift and intensity of each Si 2p surface component, we conclude that the structure of the (3×2) phase is basically the same as that of the honeycomb-chain-channel model but with a Ca coverage of 1/6 ML. Regarding the valence-band, five surface states, none of which crosses the Fermi level, were observed in the bulk band gap. 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. This result supports the proposition that the HCC structure is stabilized by the donation of two electrons per (3×2) unit cell [34]. The two other states observed in the band gap have not been reported in the literature, and they are interpreted as surface states that are peculiar to the Ca/Si(111)-(3×2) due to the 1/6 ML coverage of Ca. A new c(12×2) phase is observed in LEED after cooling the room temperature Ag/Si(111)-(6×1) phase to 100 K. In the Si 2p core-level spectra and the valence band spectra, no significant difference is observed between the two surfaces. These results indicate that the basic structure of this Ag/Si(111) surface has a c(12×2) periodicity, and that the (6×1) structure results from thermal vibrations of the surface atoms.

Acknowledgments

The authors are grateful to Dr. H. M. Zhang, Dr. H. Ashima, and Ms. W. Takeyama for their help at MAX-lab. This work was financially supported by the Swedish Research Council, the Carl Trygger Foundation, and the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.

[1] J. M. Carpinelli, H. H. Weitering, E. W. Plummer, and R. Stumpf, Nature (London) 381, 398 (1996).
[2] R. I. G. Uhrberg and T. Balasubramanian, Phys. Rev. Lett. 81, 2108 (1998).
[3] P. Segovia, D. Purdie, M. Hengsberger, and Y. Baer, Nature (London) 402, 504 (1999).
[4] H. W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schaefer, C. M. Lee, S. D. Kevan, T. Ohta, T. Nagao, and S. Hasegawa, Phys. Rev. Lett. 82, 4898 (1999).
[5] Y. Gotoh and S. Ino, Jpn. J. Appl. Phys. 17, 2097 (1978).
[6] T. Ichikawa and S. Ino, Surf. Sci. 97, 489 (1980).
[7] T. Sekiguchi, F. Shimokoshi, T. Nagao, and S. Hasegawa, Surf. Sci. 493, 148 (2001).
[8] K. Kuzmin, R.-L. Vaara, P. Laukkanen, R. E. Perälä, and I.J. Väyrynen, Surf. Sci. 538, 124 (2003).
[9] W.C. Fan and A. Ignatiev, Phys. Rev. B 41, 3592 (1990).
[10] J. Quinn and F. Jona, Surf. Sci. 248, L307 (1991).
[11] K. J. Wan, X. F. Lin, and J. Nogami, Phys. Rev. B 46, 13 635 (1992).
[12] K. J. Wan, X. F. Lin, and J. Nogami, Phys. Rev. B 47, 13 700 (1993).
[13] D. Jeon, T. Hashizume, T. Sakurai, and R. F. Willis, Phys. Rev. Lett. 69, 1419 (1992).
[14] A. A. Saranin, A. V. Zotov, V. G. Lifshts, M. Katayama, and K. Oura, Surf. Sci. 426, 298 (1999).
[15] J. J. Paggel, G. Neuhold, H. Haak, and K. Horn, Phys. Rev. B 52, 5813 (1995).
[16] T. Okuda, H. Daimon, S. Suga, Y. Tozuka, and S. Ino, Appl. Surf. Sci. 121/122, 89 (1997).
[17] H. H. Weitering, X. Shi, and S. C. Erwin, Phys. Rev. B 54, 10 585 (1996).
[18] C. Y. Park, K. S. An, J. S. Kim, R. J. Park, J. W. Chung, T. Kinoshita, A. Kakizaki, and T. Ishii, Phys. Rev. B 52, 8198 (1995).
[19] K. Sakamoto, T. Okuda, H. Nishimoto, H. Daimon, S. Suga, T. Kinoshita, and A. Kakizaki, Phys. Rev. B 50, 1725 (1994).
[20] H. H. Weitering, N. J. DiNardo, Perez-Sandoz, J. Chen, and E. J. Mele, Phys. Rev. B 49, 16837 (1994).

[21] S. Jeong and M.-H. Kang, Phys. Rev. B 54, 8196 (1996).

[22] S. C. Erwin, Phys. Rev. Lett. 75, 1973 (1995).

[23] C. Collazo-Davila, D. Grozea, and L. D. Marks, Phys. Rev. Lett. 80, 1678 (1998).

[24] S. C. Erwin and H. H. Weitering, Phys. Rev. Lett. 81, 2296 (1998).

[25] L. Lottermoser, E. Landemark, D.-M. Smilgies, M. Nielsen, R. Feidenhans’l, G. Falkenberg, R. L. Johnson, M. Gierer, A. P. Seitsonen, H. Kleine, H. Bludau, H. Over, S. K. Kim, and F. Jona, Phys. Rev. Lett. 80, 3980 (1998).

[26] M.-H. Kang, J.-H. Kang, and S. Jeong, Phys. Rev. B 58, R13359 (1998).

[27] K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, Surf. Rev. Lett. 9, 1235 (2002).

[28] H. Daimon and S. Ino, Surf. Sci. 164, 320 (1985).

[29] K. Sakamoto, W. Takeyama, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B 66, 165319 (2002).

[30] K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B 69, 045321 (2004).

[31] A. A. Baski, S. C. Erwin, M. S. Turner, K. M. Jones, J. W. Dickinson, and J. A. Carlisle, Surf. Sci. 476, 22 (2001).

[32] K. S. An, R. J. Park, J. S. Kim, C. Y. Park, C. Y. Kim, J. W. Chung, T. Abukawa, S. Kono, T. Kinoshita, A. Kakizaki, and T. Ishii, Surf. Sci. 337, L789 (1995).

[33] T. Okuda, H. Ashima, H. Takeda, K. S. An, A. Harasawa, and T. Kinoshita, Surf. Sci. 282, 17 (1993).

[34] G. Lee, S. Hong, H. Kim, D. Shin, J.-Y. Koo, H.-I. Lee, and D. W. Moon, Phys. Rev. Lett. 87, 056104 (2001).

[35] H. H. Weitering, Phys. Rev. B 64, 165312 (2001).

[36] D. Y. Petrovykh, K. N. Altmann, J.-L. Lin, F. J. Himpsel, and F. M. Leibsle, Surf. Sci. 512, 269 (2002).

[37] O. Gallus, Th. Pillo, P. Starowicz, and Y. Baer, Europhys. Lett. 60, 903 (2002).

[38] Y. K. Kim, J. W. Kim, H. S. Lee, Y. J. Kim, and H. W. Yeom, Phys. Rev. B 68, 245312 (2003).

[39] J. Ihm, M. L. Cohen, and J. R. Chelikowsky, Phys. Rev. B 22, 4610 (1980).

[40] F. J. Himpsel, G. Hollinger, and R. A. Pollak, Phys. Rev. B 28, 7014 (1983).

[41] T. Okuda, K. Sakamoto, H. Nishimoto, H. Daimon, S. Suga, T. Kinoshita, and A. Kakizaki, Phys. Rev. B 55, 6762 (1997).

[42] R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, P. E. S. Persson, and S. A. Flocström, Phys. Rev. B 31, 3805 (1985), and references therein.

[43] K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B 68, 245316 (2003).

[44] J. Schäfer, S. C. Erwin, M. Hansmann, Z. Song, E. Rotenberg, S. D. Kevan, C. S. Hellberg, and K. Horn, Phys. Rev. B 67, 085411 (2002).

[45] K. Sakamoto, H. Ashima, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B 65, 045305 (2002).

[46] R. J. Wilson and S. Chiang, Phys. Rev. Lett. 58, 369 (1987).

[47] J. M. Carpinelli and H. H. Weitering, Phys. Rev. B 53, 12651 (1996).

[48] J. M. Carpinelli and H. H. Weitering, Surf. Sci. 331-333, 1015 (1995).

[49] H. Ohnishi, Y. Yamamoto, I. Katayama, Y. Ohba, and K. Oura, Appl. Surf. Sci. 82/83, 444 (1994).

[50] K. Kempa, D. A. Broido, and H. H. Weitering, Physica B 230-232, 800 (1997).

[51] G. Le Lay, M. Göthelid, A. Cricenti, C. Hakansson, and P. Perfetti, Europhys. Lett. 45, 65 (1998).

[52] See for example, T. Takahashi and S. Nakatani, Surf. Sci. 282, 17 (1993).

[53] E. Landemark, C. J. Karlsson, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. Lett. 69, 1588 (1992).

[54] See for example, R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B 34, 5343 (1986).

[55] Y. Ena, S. Suzuki, and S. Kono, Phys. Rev. Lett. 65, 2704 (1990).