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Identification of the basic structure of the Ag/Si(111)-(6×1) surface: Observation of a low-temperature $c(12\times 2)$ phase

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The surface structure of the so-called Ag/Si(111)-(6×1) surface is studied by low-energy electron diffraction (LEED), high-resolution core-level photoelectron spectroscopy, and angle-resolved photoelectron spectroscopy. A $c(12\times 2)$ phase is observed in LEED after cooling the room-temperature (6×1) phase to 100 K. In the Si 2*p* core-level spectra, no significant difference is observed between the two surfaces. In the valence-band spectra, five surface states are observed on both the (6×1) and $c(12\times 2)$ surfaces. None of these surface states crosses the Fermi level. The binding energies and dispersions of the surface states observed on the (6×1) surface are quite similar to those of the $c(12\times 2)$ surface. These results indicate that the basic structure of this Ag/Si(111) surface has a $c(12\times 2)$ periodicity, and that the (6×1) structure results from thermal vibrations of the surface atoms. Moreover, we assign two of the surface states to bonding states between Ag and Si atoms, and one of them to a π -bond state.

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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. These nanoscale structures are quite nice systems for the study of low-dimensional physics, e.g., phase transitions in one- or two-dimensional systems,¹ and they are also of a profound interest from the technological point of view.

Among the great number of metal induced surface reconstructions, the Si(111)-(3×1) surface is one of the most well known. This Si(111)-(3×1) surface is formed by various adsorbates, e.g., alkali metals, alkaline-earth metals, rare-earth metals (Sm and Yb), and Ag with a coverage of 1/3 ML. Although some of the adsorbates actually show different diffraction patterns, e.g., Ag shows a (6×1) pattern,^{2,3} 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,^{4,5} scanning-tunneling-microscopy (STM) images,⁶⁻⁹ and surface core-level shift (SCLS) measurements.^{8,10,11} The atomic geometry of 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.^{9,12} Recently, a model that is energetically more stable than the former ones was reported independently by several groups.¹³⁻¹⁵ This model, called the honeycomb-chain-channel (HCC) model,¹³⁻¹⁵ is fully compatible with the SCLS results and the STM images.

The electronic character is stated to be semiconducting for Li,¹¹ Na,¹⁶ K,¹⁷ and Mg¹⁸ adsorbed Si(111)-(3×1) surfaces by angle-resolved photoelectron spectroscopy (ARPES). This semiconducting character agrees well with the scanning tunneling spectroscopy (STS) study, in which a gap of approximately 1 eV is obtained for a Na/Si(111)-(3×1) surface.⁷ Moreover, several surface states are observed in the band gap and pockets of the bulk band projection in the

ARPES studies.^{11,16-18} Using theoretical calculations, the two surface states situated in the band gap are attributed to the bonding states between the adsorbate and the surface Si atoms.^{13,15}

In the case of the Ag/Si(111)-(6×1) surface, the structure is reported to originate from a slight displacement of the surface atoms of the (3×1) structure.³ This report is based on the observation of the (3×1)↔(6×1) transition at a temperature of approximately 500 K.^{2,3} Using STM, both (3×1) (Refs. 6 and 19-21) and (6×1) (Refs. 9, 20, and 21) structures are observed at 300 K. Taking into account the observation of a tip-induced (3×1)→(6×1) transition,²⁰ the (6×1) structure is suggested to be the stable phase, and the (3×1) structure a metastable one. This idea is supported by a theoretical calculation,²² 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.

In this paper, we present temperature-dependent LEED, high-resolution Si 2*p* core-level, and ARPES studies of the Ag/Si(111)-(6×1) surface. After cooling the surface to 100 K, a $c(12\times 2)$ pattern is observed in LEED. In the Si 2*p* core-level study, no significant difference is observed between 300 and 100 K. These results indicate a strong similarity between the atomic structures of the (6×1) and $c(12\times 2)$ phases. In the ARPES study, five surface states with negligible dispersion are clearly observed in the gap, and pockets of the bulk band projection on both surfaces. Since none of the surface states crosses the Fermi level, we conclude that both Ag/Si(111)-(6×1) and $c(12\times 2)$ surfaces

have semiconducting characters.

II. EXPERIMENTAL DETAILS

The high-resolution photoemission measurements and LEED studies were performed at beamline 33 at the MAX-I synchrotron radiation facility in Lund, Sweden. The photoemission spectra were obtained with an angle-resolved photoelectron spectrometer with an angular resolution of $\pm 2^\circ$. The total-energy resolutions were ~ 80 and ~ 50 meV for the Si $2p$ core-level and valence-band measurements, respectively. The Si(111) sample, cut from a Sb-doped (n -type) Si wafer, was preoxidized chemically before it was inserted into the vacuum system. We annealed the sample at 1230 K by direct resistive heating in the vacuum chamber to remove the oxide layer, and at 1520 K to remove carbon contamination from the surface. After the annealing, we observed a sharp (7×7) LEED pattern, and neither the valence-band spectra nor the Si $2p$ core-level spectra showed any indication of contamination. To make a Ag/Si(111)- (6×1) surface, we first formed a Ag/Si(111)- $(\sqrt{3} \times \sqrt{3})$ surface by annealing a surface covered with 1.0 ML of Ag at approximately 700 K, and then gently annealed the sample at a temperature between 850 and 900 K. Neither evaporation of Ag on the Si(111) surface at a temperature between 850 and 900 K nor annealing of the sample after adsorption of 1/3 ML of Ag at 300 K was successful to obtain an entirely uniform (6×1) surface.

III. RESULTS

A. LEED

Figure 1(a) shows the LEED pattern of a three domain Ag/Si(111)- (6×1) surface, obtained with a primary electron energy (E_p) of 58 eV at 300 K. The $\times 6$ spots observed in Fig. 1 did not show up immediately after annealing the sample at 850 K, i.e., they only appear upon cooling the sample close to room temperature. This result agrees well with the previous studies,^{2,3} in which the $(3 \times 1) \rightarrow (6 \times 1)$ phase transition is reported to occur near 500 K. Since the surface has both stable (6×1) and metastable (3×1) phases at 300 K,^{20,22} we cooled down the sample to a lower temperature to obtain a more stable surface. Figure 1(b) shows the LEED pattern obtained with $E_p = 58$ eV at 100 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. 1(b) with the schematic pattern of Si(111)- $c(12 \times 2)$ [Fig. 1(c)], we conclude that the surface structure has transformed to a $c(12 \times 2)$ structure at 100 K.

B. Si $2p$ core level

In order to understand the origin of the $(6 \times 1) \rightarrow c(12 \times 2)$ phase transition, we have measured the Si $2p$ core level at 300 and 100 K. The uppermost Si $2p$ core-level spectrum in Fig. 2 was recorded at 300 K for a Ag/Si(111)- (6×1) surface. The photon energy ($h\nu$) is 130 eV, and the emission angle (θ_e) of the photoelectrons is 0° , i.e., the surface normal direction. We also show the corresponding spectrum ob-

FIG. 1. LEED pattern of the three-domain Ag/Si(111)- (6×1) surface obtained with $E_p = 58$ eV at 300 K (a). The LEED pattern obtained with the same E_p at 100 K is displayed in (b). (c) shows the schematic LEED pattern of a three domain Si(111)- $c(12 \times 2)$ surface.

tained from the low temperature Ag/Si(111)- $c(12 \times 2)$ surface in Fig. 2, together with spectra taken at different $h\nu$ and θ_e that give a difference in the surface sensitivity. For the most surface sensitive measurement, we have used $h\nu = 130$ eV and $\theta_e = 60^\circ$. A rigid shift of 0.45 eV toward a higher binding energy, which is observed after cooling the sample to 100 K, results from the surface photovoltage effect.²³ The spectra in Fig. 2 look different from those observed previously.^{10,24} That is, the peak indicated by a dashed line has not been observed in the previous Si $2p$ core-level studies.^{10,24} This difference might come from the lower resolution of the experimental setups and/or a different quality of the samples used in these studies.

By comparing the two spectra obtained with $h\nu = 130$ eV and $\theta_e = 0^\circ$ at 300 and 100 K [Figs. 2(a) and 2(b)], we find that the Si $2p$ core-level spectra of the Ag/Si(111)- (6×1) and Ag/Si(111)- $c(12 \times 2)$ surfaces are quite similar. To discuss the similarity in more detail, we consider the components that contribute to the spectra. Without any processing, the spectra shown in Fig. 2 reveal the presence of several components that contribute to the shape of the spectra. The most evident one is $S1$ which is revealed by its $2p_{1/2}$ component. The $2p_{1/2}$ component of $S1$ is indicated by a dashed line, and it is clearly observed as a peak at several $h\nu$. The presence of $S2$ is confirmed by the behavior of the valley between the $2p_{3/2}$ and $2p_{1/2}$ components of B. That is, comparing the spectra obtained with $h\nu = 130$ and 145 eV, the valley is shallower at 145 eV though the intensity of $S1$ is weaker. This shallower valley indicates the presence of another component situated between the $2p_{3/2}$ and $2p_{1/2}$ of B. The $S3$ component is recognized by the extension of the

FIG. 2. Si $2p$ core-level spectrum of the Ag/Si(111)-(6 $\times$ 1) surface measured at 300 K with $h\nu=130$ eV (a). The spectra of the Ag/Si(111)-c(12 $\times$ 2) surface measured at 100 K using different $h\nu$ and θ_e are displayed from (b) to (f). The spectra from (a) to (e) were measured at $\theta_e=0^\circ$, while (f) was obtained at $\theta_e=60^\circ$. The solid lines indicate the energy positions of the Si $2p_{3/2}$ parts of the four major components, and the dashed line the Si $2p_{1/2}$ part of the S1 component.

tail at the right side of the $2p_{3/2}$ component of B observed in the spectra obtained at a higher surface sensitivity.

C. Valence band

In Fig. 3, we show the valence-band photoelectron spectrum of a Ag/Si(111)-(6 $\times$ 1) surface in (a), and those of surfaces where the (6 $\times$ 1) and ($\sqrt{3}\times\sqrt{3}$) phases coexist in (b) and (c). The incidence photon angle is 55° , and the emission angle (θ_e) of the photoelectrons is 6° from the surface normal along the $[1\bar{1}0]$ direction. The Fermi-level position (E_F), which is indicated by a dashed line, was determined by measuring the metallic Fermi edge of a Ta foil fixed on the sample holder. In LEED, the sample used for Fig. 3(c) showed brighter ($\sqrt{3}\times\sqrt{3}$) spots than those of the sample used for (b). A difference in brightness of the ($\sqrt{3}\times\sqrt{3}$) spots suggests a different ratio of the ($\sqrt{3}\times\sqrt{3}$) to the (6 $\times$ 1) area, and thus a larger area of the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$) domain is expected for the sample in (c) compared to the sample in (b). Comparing the three surfaces, we notice a drastic change in the Ag $4d$ band region, i.e., around a bind-

FIG. 3. Valence-band photoelectron spectrum of a Ag/Si(111)-(6 $\times$ 1) surface (a), and those of surfaces where (6 $\times$ 1) and ($\sqrt{3}\times\sqrt{3}$) phases coexist [(b) and (c)], measured at a sample temperature of 300 K. Sample (c) showed brighter ($\sqrt{3}\times\sqrt{3}$) LEED spots than sample (b).

ing energy (E_B) of 5 eV, and the growth of peaks at $E_B=1.0$, 2.0 and 3.9 eV as the area of the ($\sqrt{3}\times\sqrt{3}$) phase increases. The binding energies of 1.0 and 2.0 eV agree well with those of the surface states of a Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface.²⁵ On a complete Ag/Si(111)-(6 $\times$ 1) surface, the main peak of the Ag $4d$ level is located at $E_B=5.1$ eV. On a surface for which LEED shows a comparable brightness for the (6 $\times$ 1) and ($\sqrt{3}\times\sqrt{3}$) spots, the main $4d$ component has a large peak at $E_B=5.9$ eV with a shoulder at $E_B=5.1$ eV. On a surface with a smaller ($\sqrt{3}\times\sqrt{3}$) area, two peaks are clearly observed at $E_B=5.1$ and 5.9 eV. This result suggests that the binding energies of the Ag $4d$ bands have a difference of 0.8 eV between the Ag/Si(111)-(6 $\times$ 1) and ($\sqrt{3}\times\sqrt{3}$) surfaces, and that the binding energies and also the shape of the Ag $4d$ bands are good indicators of the surface quality.

Figure 4 shows the valence-band photoelectron spectra of three-domain Ag/Si(111)-(6 $\times$ 1) and Ag/Si(111)-c(12 $\times$ 2) surfaces measured at $\theta_e=0^\circ$, 20° , and 40° along both the $[1\bar{1}0]$ and $[11\bar{2}]$ directions. The solid and dashed lines correspond to the spectra of the Ag/Si(111)-(6 $\times$ 1) and c(12 $\times$ 2) surfaces, respectively. The light beam, polarization vector, and detector were all in the plane defined by the surface normal and the $[1\bar{1}0]$ direction, for the measurements along the $[1\bar{1}0]$ direction. For the measurements along the $[11\bar{2}]$ direction, we have moved the detector in the vertical plane. The spectra of the Ag/Si(111)-(6 $\times$ 1) and c(12 $\times$ 2) surfaces along both the $[1\bar{1}0]$ and $[11\bar{2}]$ directions are very similar. This result indicates that the Ag/Si(111)-c(12 $\times$ 2) surface is not formed by gas adsorption during the cooling, since adsorption of residual gases should change the electronic structure. Further, both hydrogen and oxygen have strong photoemission features in a binding-energy range from 5 to 7 eV,

FIG. 4. Valence-band photoelectron spectra of three-domain Ag/Si(111)-(6 $\times$ 1) and c (12 $\times$ 2) surfaces measured at emission angles of 0°, 20°, and 40° along the [110] and [112] directions. Solid and dashed lines correspond to the Ag/Si(111)-(6 $\times$ 1) and the Ag/Si(111)- c (12 $\times$ 2) surfaces, respectively.

but no additional features were observed in this binding energy region after cooling the sample.

IV. DISCUSSION

A. Surface structure

A quantitative information for the structures of the Ag/Si(111)-(6 $\times$ 1) and c (12 $\times$ 2) surfaces, is obtained by analyzing the spectra in Fig. 2 by a standard least-squares-fitting method using spin-orbit split Voigt functions. Figure 5 shows the results of the analysis for the Si 2 p core-level spectra of the Ag/Si(111)-(6 $\times$ 1) and c (12 $\times$ 2) surfaces obtained at $h\nu=130$ eV. θ_e is 0° in (a) and (b), and 60° in (c). The open circles are the experimental data, and the solid lines overlapping the data are the fitting curves. We used 605 meV

FIG. 5. Decomposition of the Si 2 p core-level spectra of the Ag/Si(111)-(6 $\times$ 1) surface measured at 300 K in (a), and the Ag/Si(111)- c (12 $\times$ 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).

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 are 217 and 212 meV (FWHM) for the (6 $\times$ 1) and c (12 $\times$ 2) surfaces, respectively. The other parameters used in the fitting procedure are shown in Table I. A polynomial background was subtracted before the decomposition of each spectrum, and each component is indicated by different hatching.

From the result of the fitting procedure, we can conclude that both the Ag/Si(111)-(6 $\times$ 1) and c (12 $\times$ 2) surfaces have

TABLE I. Energy shifts and intensities of the surface components relative to the bulk Si 2 p component. The Gaussian width (FWHM) of each surface component is also tabulated.

		S1	S2	S3
300 K, 0°	energy (meV)	424	145	-129
	intensity	0.478	0.512	0.285
	Gaussian (meV)	228	245	239
100 K, 0°	energy (meV)	430	143	-115
	intensity	0.454	0.451	0.183
	Gaussian (meV)	225	238	225
100 K, 60°	energy (meV)	433	150	-123
	intensity	0.694	0.795	0.183
	Gaussian (meV)	225	238	225

FIG. 6. LEED pattern of a Ag/Si(111) surface on which the (6×1) and $(\sqrt{3} \times \sqrt{3})$ phases coexist. $E_p = 80$ eV, and the sample temperature was 300 K.

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 a clean Si(001) surface.²⁶ That is, the room temperature Si(001)- (2×1) and low-temperature $c(4 \times 2)$ phases show very similar Si $2p$ spectra, and they have surface components with the same energy shifts.²⁶ 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 dimers²⁷ at a high frequency. Since the translational vectors of the $c(12 \times 2)$ 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. Hence we conclude that the basic unit cell of the so-called Ag/Si(111)- (6×1) surface has a $c(12 \times 2)$ periodicity, and the (6×1) phase results from the thermally induced disorder of the atomic displacements of the $c(12 \times 2)$ structure.

To support this picture, we observed the LEED pattern of a surface where the (6×1) and $(\sqrt{3} \times \sqrt{3})$ phases coexist at 300 K. Figure 6 shows the LEED pattern of the mixed Ag/Si(111)- (6×1) and $(\sqrt{3} \times \sqrt{3})$ surface obtained with $E_p = 80$ eV at 300 K. Besides the spots from the (6×1) and $(\sqrt{3} \times \sqrt{3})$ structures, weak $\times 2$ streaks reveal the presence of the $c(12 \times 2)$ structure with frequent phase mismatching. The phase mismatching of the $c(12 \times 2)$ 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 $c(12 \times 2) \rightarrow (6 \times 1)$ conversion.

In order to discuss the origins of the surface components shown in Fig. 5, we assume that the structure of the Ag/Si(111)- $c(12 \times 2)$ surface is basically the same as that of the HCC model,^{13,15} but with a slight displacement of Ag and/or top-layer Si atoms to introduce the necessary atomic displacements. In the Si $2p$ core-level spectrum of the Ag/

Si(111)- $(\sqrt{3} \times \sqrt{3})$ surface,²⁸ 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)- $(\sqrt{3} \times \sqrt{3})$ surface²⁹ with that of the HCC model,¹³⁻¹⁵ 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)- $c(12 \times 2)$ surfaces. Since a smaller charge transfer leads to a smaller energy shift for the surface component, we assign the S2 component to Si atoms bonded directly to the Ag atoms. In order to make an assignment of the S1 and S3 components, we compare the Si $2p$ spectra obtained at different emission angles, i.e., Figs. 5(b) and 5(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 corresponds 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,¹³⁻¹⁵ we assign S1 to the Si atoms in the top layer not bonded to Ag. Moreover, these Si atoms are suggested to rehybridize into a sp^2 and p_z orbitals^{13,15} and form π bonds. The energy shift of these π -bonded Si atoms is reported to be approximately +370 meV by a theoretical calculation,¹⁵ which supports our assignment of the S1 component.

B. Electronic structure

In order to obtain clearer information on the surface electronic states, we have measured the angle-resolved photoelectron spectra of the Ag/Si(111)- (6×1) and $c(12 \times 2)$ surfaces at every 2.5° from $\theta_e = 0^\circ$ to 40° , and at every 5.0° for angles larger than 40° along both the $[1\bar{1}0]$ and $[11\bar{2}]$ directions. For the Ag/Si(111)- $c(12 \times 2)$ surface, we have also measured the spectra at every 4° . Here, we have to recognize that due to the threefold symmetry of the Si(111) substrate, we obtain three orientations of the surface Brillouin zones (SBZ's) for both (6×1) and $c(12 \times 2)$ surfaces that are rotated azimuthally. Figure 7(a) shows the SBZ's of a Si(111)- (1×1) surface, and single-domain (6×1) and $c(12 \times 2)$ surfaces. The thin solid line represents the SBZ of the (1×1) surface, and the thick dashed and solid lines are the SBZ's of the (6×1) and $c(12 \times 2)$ surfaces. The symbols $\bar{\Gamma}$, $\bar{M}$, and $\bar{K}$ are the symmetry points of the (1×1) SBZ. In Fig. 7(b), we display the three orientations of the SBZ's that differ by 120° . Accordingly, the spectra measured along the $[1\bar{1}0]$ direction contain not only information about the surface state dispersion along the $\bar{\Gamma}$ - $\bar{K}$ direction of the (1×1) surface, but also information along the direction labeled A, regarding the SBZ's of the (6×1) and $c(12 \times 2)$ surfaces, is obtained. Likewise the spectra measured along the $[11\bar{2}]$ direction contain information along the $\bar{\Gamma}$ - $\bar{M}$ direction of the (1×1) surface and the direction labeled B for the SBZ's of the (6×1) and $c(12 \times 2)$ surfaces.

FIG. 7. Surface Brillouin zones of the Si(111)-(1 $\times$ 1), (6 $\times$ 1), and c (12 $\times$ 2) surfaces are indicated by thin solid lines, thick dashed lines, and thick solid lines, respectively, in (a). (b) shows the three orientations of the surface Brillouin zones of the (6 $\times$ 1) and c (12 $\times$ 2) surfaces that differ by 120°.

Figures 8(a) and 8(b) display the band maps along the $[1\bar{1}0]$ and $[11\bar{2}]$ directions, respectively. The open circles represent the peak and shoulder positions observed in the valence-band photoelectron spectra of the Ag/Si(111)-(6 $\times$ 1) surface, and the filled ones are those of the Ag/Si(111)- c (12 $\times$ 2) surface. Three different sizes of the circles have been used to indicate the intensity of the peaks and shoulders. The shaded area is the bulk band projection taken from Ref. 30. The valence-band maximum (VBM) is estimated from the binding energy of the Si 2 p core level using the relation among $E_{B(\text{VBM})}$, E_F , and $E_{B(\text{Si}2p_{3/2})}$ given in Ref. 31. 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 alkali and alkaline-earth metals adsorbed Si(111)-(3 $\times$ 1) surfaces,^{11,16–18} 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 $\times$ 1) and c (12 $\times$ 2) surfaces, while values between 0.4 and 0.7 eV are found for alkali and alkaline-earth metals adsorbed Si(111)-(3 $\times$ 1) surfaces.^{11,16–18} In Na- and K-adsorbed Si(111)-(3 $\times$ 1) studies,^{16,17} in which three equivalent (3 $\times$ 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

FIG. 8. Band dispersion of the Ag/Si(111)-(6 $\times$ 1) and c (12 $\times$ 2) surfaces measured along the $[1\bar{1}0]$ direction in (a), and the $[11\bar{2}]$ direction in (b). The open circles represent the peak and shoulder positions obtained in the valence-band photoelectron spectra of the Ag/Si(111)-(6 $\times$ 1) surface, and the filled ones are those of the Ag/Si(111)- c (12 $\times$ 2) surface. Three different sizes of 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.

structures. Hence we conclude that both the Ag/Si(111)-(6 $\times$ 1) and c (12 $\times$ 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 $\times$ 1) or the Ag/Si(111)- c (12 $\times$ 2) surface. This result suggests a completely semiconducting character of the two surfaces, and it agrees well with the STS study²⁰ in which a gap of 0.9 eV is observed for the Ag/Si(111)-(6 $\times$ 1) surface.

Regarding the binding energy and dispersion, no obvious difference is observed between the surface states of the Ag/Si(111)-(6 $\times$ 1) surface and those of the Ag/Si(111)- c (12 $\times$ 2) surface. Such a result for surface states of different surface structures is also observed on the clean Si(001) surface.³² That is, the surface states of the room-temperature Si(001)-(2 $\times$ 1) phase and those of the low-temperature c (4 $\times$ 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)- $c(12\times 2)$ 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 $c(12\times 2)$ surfaces.

Finally, we discuss the origins of the S_1 , S_2 , and S_3 states. Among the surface states observed experimentally on alkali and alkaline-earth metals adsorbed Si(111)-(3×1) surfaces,^{11,16–18} the origins of the three with the smallest binding energies are explained by theoretical calculations using the HCC model.^{13,15} 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. The observation of two alkali-metal–Si bonding states results from the presence of two different alkali-metal–Si bonding configurations in the HCC model. Assuming that the structure of the Ag/Si(111)- $c(12\times 2)$ surface is basically the same as that of the HCC model,^{13–15} 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 alkali and alkaline-earth metals adsorbed Si(111)-(3×1) is expected. Since the π -bond state is located at approximately $E_B = 2$ eV on both Na (Ref. 16) and K (Ref. 17) adsorbed Si(111)-(3×1) 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 alkali and alkaline-earth metals adsorbed Si(111)-(3×1) surfaces, all surface states, which originate from the surface Si atoms only, have binding energies higher than 2 eV. Hence we conclude that the origins of S_1 and S_2 are the Ag–Si bond with different configurations. As we mentioned above, the structures of Ag/Si(111)-(6×1) and $c(12\times 2)$ 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 $c(12\times 2)$ 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.

V. CONCLUSION

In conclusion, we have studied the surface structure of the Ag/Si(111)-(6×1) surface by means of LEED, high-resolution core-level photoelectron spectroscopy, and ARPES. The (6×1) LEED pattern observed at 300 K, has changed to a $c(12\times 2)$ pattern at 100 K. Taking into account that there is no significant difference between the Si $2p$ core-level spectra and the valence-band spectra for the (6×1) and $c(12\times 2)$ surfaces, we conclude that the basic structure of the surface has a $c(12\times 2)$ periodicity and that the appearance of a (6×1) structure is a result of thermally induced disorder. The weak $\times 2$ streaks observed in LEED on the mixed Ag/Si(111)-(6×1) and ($\sqrt{3}\times\sqrt{3}$) surface at 300 K supports our picture. The three surface components observed in the Si $2p$ core-level spectra are assigned to the top-layer Si atoms bonded to Ag, Si atoms of the top layer which form π bonds, and the second-layer Si atoms, respectively. In the ARPES study, five surface states with negligible dispersion are observed in the gap and pockets of the bulk band projection on both the (6×1) and $c(12\times 2)$ surfaces. Among the five surface states observed in the valence-band spectra, S_1 and S_2 are assigned to the bonding states between Ag and Si atoms, and the S_3 state to the π -bond state. Moreover, no Fermi-level crossing is observed in the valence band spectra, indicating a completely semiconducting character of the Ag/Si(111)-(6×1) and $c(12\times 2)$ surfaces.

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