Electronic structures of the Si(001)2×3-Ag surface

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Electronic structures of the double- and single-domain Si(001)2×3-Ag surfaces were investigated by angleresolved photoelectron spectroscopy using synchrotron radiation. All the surface states related to Si dimers are shown to disappear upon forming the 2×3-Ag phase. Instead, five surface-state bands are identified within the bulk band gap with binding energies 0.8–2.6 eV, whose dispersions are determined for symmetric lines of the surface Brillouin zone. The Si(001)2×3-Ag surface is clearly shown to be semiconducting with a band gap larger than 0.8 eV. This result can be in significant conflict with the presently available structure models of this surface phase. [S0163-1829(98)01907-9]

I. INTRODUCTION

Noble-metal, especially Ag, adsorption on Si surfaces has been at the center of the efforts to understand the fundamental physical properties of metal/semiconductor interfaces and metal ultrathin films on semiconductor surfaces during the past two decades.^{1,2} This is mainly due to the chemical nonreactivity of Ag with Si and the formation of well-defined interfaces. Apart from this fundamental issue, there has been great technological interest in Ag/Si systems for the ideal metal contact, Shottkey barrier formation, and more recently the potential of quantum devices.³ Despite the great importance of Ag/Si interfaces, the early stage growth of Ag on the Si(001) surface has received very little attention. This is in sharp contrast to the extensively studied Ag/Si(111) system.² This had been partly due to the absence of well-ordered phases reported for the early stage growth of Ag on the Si(001) surface until very recently. Recent scanning tunneling microscopy^{4,5} (STM) and low-energy electron diffraction⁶ (LEED) observations of a few ordered phases, such as 2×3 , 4,5 2×1 , 4,5 and $c(6 \times 2)$, 6 have revived a wide interest in the microscopic structures of Ag adsorption on Si(001).

However, the structures of the surface phases formed by Ag adsorption on the Si(001) surface are still uncertain, although several structure models have been proposed for the 2×3 (Ref. 7) and the 2×1 (Ref. 7) phases. In addition to the structures of these surface phases, there are interesting relevant issues in the growth of Ag on Si(001) such as the surface unwetting,⁸ the domain ordering,⁹ and unusual island structures.¹⁰ Most of these issues are very closely related to the detailed surface structures and the characteristics of the bonding between Ag and Si at the interface/surface. This naturally leads to an urgent need for a detailed surface electronic structure study along with surface structure determination of the Ag-induced phases on Si(001), which has not been available so far.

This paper reports an electronic-structure study of the rather well known 2×3 phase of submonolayer Ag adsorption on the Si(001) 2×1 surface. To our knowledge, this is

the first such study for any of the ordered surface phases of Ag adsorption on the Si(001) surface. Employing angleresolved photoelectron spectroscopy (ARPES) using synchrotron radiation, several intrinsic surface states are identified and their dispersions are determined. The implication of this result on the surface structure models is discussed.

II. EXPERIMENT

The ARPES measurements were done on the beam line BL-7B of Research Center for Spectrochemistry of the University of Tokyo in Photon Factory, Japan. The beam line has a Seya-Namioka–type monochrometer to deliver photon beams with energy $(h\nu)$ of 5–40 eV.¹¹ It is equipped with a commercial angle-resolved photoelectron spectrometer (VG ADES 400). The base pressure of this system was ~5 $\times 10^{-11}$ mbar during the experiment. The overall angular and energy resolutions chosen were ~1.5° and ~160 meV, respectively.

A mirror-polished and accurately oriented Si(001) wafer $(25 \times 3.5 \times 0.38 \text{ mm}^3)$ was used to produce a single-domain (SD) 2×1 surface with very wide terraces. A SD Si(001) 2×1 surface was prepared by preoxidation and cycles of *in* situ heat treatments. The fraction of minor domain could be kept below 10% of the major domain as estimated from the intensity ratio of corresponding LEED spots. Details of this procedure can be found elsewhere.¹² Deposition of Ag was done using a graphite effusion cell. The pressure during deposition was kept below $\sim 5 \times 10^{-10}$ mbar. The evolutions of LEED patterns during deposition of Ag at different substrate temperatures were the same as recently reported.⁶ In brief, the 2×1 LEED pattern persists over ~ 2 ML at roomtemperature deposition and the best SD $c(6 \times 2)$ and doubledomain (DD) 2×3 LEED patterns are acquired at a Ag coverage of $\sim 0.6 \text{ ML}$ after postannealings of $\sim 200 \,^{\circ}\text{C}$ and \sim 350 °C, respectively. The so-called SD 2×3 LEED pattern⁶ is developed by a deposition of ~ 0.6 ML at a substrate temperature of ~ 200 °C. The SD 2×3 and DD 2×3 phases were found to have the same local structure by x-ray photoelectron diffraction.⁶

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FIG. 1. (a) Essential geometry of an ARPES measurement and the definitions of the angles used. (b) The 2×3 SBZ with symmetry points marked. The SBZ and symmetry points for the clean Si(001) 2×1 surface are also given together (dashed lines and bold letters in parentheses, respectively).

Photoemission measurements were done on the SD 2×3 and DD 2×3 phases formed at the same Ag coverage. ARPES spectra were taken at a step of $\sim 2^{\circ}$ in the emission angle (θ_{e}) [see Fig. 1(a)] along the most important symmetric axes of the 2×3 surface Brillouin zone (SBZ) shown in Fig. 1(b). Linearly polarized synchrotron radiation was used at $h\nu$'s of 17.6 and 21.9 eV at an incidence angle (θ_i) of 45° from the surface normal [Fig. 1(a)]. The Fermi level (E_F) was determined from the surface of a well cleaned Ta plate in good electric contact with the Si sample. All spectra shown below are normalized by background intensities above E_F , which are proportional to the actual photon flux on the sample surface.^{13,14} In order to help assign the Aginduced spectral features through comparison, detailed ARPES spectra of the clean SD Si(001) 2×1 surface were also measured using the same sample and $h\nu$'s.¹⁵

III. ARPES RESULTS

Figure 2(a) gives an overview of the drastic changes in valence bands due to formation of the 2×3 -Ag phase. At first look, we can see the prominent contribution from Ag 4*d* levels around a binding energy (BE) $E_B \approx 6$ eV. The appearance of two other features, denoted as S_1 and S_3 in the figure, with $E_B < 2$ eV is also distinctive in the spectra of the 2×3 phase. These two lower-BE features replace the well known surface state of the clean surface, denoted as *A* following the convention of Ref. 16. Considering their BE's and in comparison to clean surface spectra, S_1 and S_3 are most likely due to new surface states of the 2×3 phase as discussed below. For the discussion hereinafter, we will concentrate only on the spectral features with $E_B < 5$ eV excluding the Ag 4*d* contribution and any other possible higher-BE surface states/resonances.

One set of detailed ARPES spectra for the DD 2×3 surface is shown in Fig. 3. These spectra are taken along the diagonal azimuth [010] [see Fig. 1(b)], where contributions from the two 90°-rotated domains are identical. Since the [010] azimuth has the widest bulk band gap (up to $E_B \sim 3.6 \text{ eV}$ around $\theta_e \sim 40^\circ$; see Fig. 4 for the bulk band edge), it is relatively easy to identify a surface state. One of the



FIG. 2. Typical ARPES spectra for the DD Si(001)2×3-Ag (dots) and clean SD Si(001)2×1 (lines) surfaces taken with (a) $h\nu$ =21.9 eV at normal emission (θ_e =0°) along the [110] azimuth and (b) $h\nu$ =17.6 eV at θ_e =40° along the [010] azimuth. The incidence angle of photon (θ_i) is 45°. Surface-state and bulk-related peaks (see the text) assigned are marked for both surfaces.

most prominent features in this figure is that due to the wellknown bulk direct transition (denoted as band *b* in the figure), which is close to the edge of the bulk band gap.¹⁶ By comparing the BE of this bulk band with that observed on the clean surface as shown in Fig. 2(b), it is possible to estimate the amount of band bending. The corresponding BE shift is ~0.05 eV, that is, almost no change in band bending for the 2×3 phase from the clean surface. Accordingly, the valence-band maximum is estimated to be located at $E_B \approx 0.65$ eV for the 2×3-Ag surface.

Within the band gap, roughly above the bulk band b, we can find five different spectral features denoted as S_1 , S_2 , S_3 , S_4 , and S'_4 [see Figs. 2(b) and 3], which are marked with different symbols in Fig. 3. The lowest-BE state S_1 has rather large intensity around the normal emission but is barely observed in the range $28^\circ < \theta_e < 40^\circ$. This state is very close to another parallel band of S_2 , which appears strong in the θ_e range 8°–28°. S_1 and S_2 have very similar BE's to those of the dangling-bond surface states of the clean surface [Fig. 2(b)].¹⁶ Below S_1 and S_2 there are big bumps in the spectra within the gap. A close look of these bumps leads to the identification of three different spectral features denoted as S_3 , S_4 , and S'_4 bands. Since S_3 shows almost no dispersion in the gap region, it is very likely to be connected to the weak features out of the gap around the normal emission at the same BE of $\sim 1.8 \text{ eV}$ (open triangles in Fig. 3). The comparison with clean surface spectra, shown in Fig. 2(b) for example, obviously indicates that these five states replaced all the surface states related to Si dimers on the clean surface¹⁶ within the bulk band gap. Another conspicuous feature observed in the spectra along [010] is the dispersing band S_5 at $E_B \sim 4$ eV.

Dispersions of the bands observed are shown in Fig. 4 in detail. S_1 , S_2 , and S_3 are shown to have very small disper-



FIG. 3. Normalized ARPES spectra for the DD Si(001)2×3-Ag surface taken with $h\nu$ =17.6 eV along the [010] azimuth. The step in emission angles (θ_e) is 2° and the incidence angle of photon (θ_i) is 45°. The peak positions for different surface-state bands assigned (see the text) are marked with different symbols.

sions less than $\sim 0.2 \text{ eV}$. Due to their presence well within the bulk band gap, the five bands $S_1 - S'_4$ can be assigned as surface states. Since the bulk band features in ARPES spectra of the Si(001) surface is well established, 16 it is clear that these states are not related to bulk direct transitions. We measured ARPES spectra of the clean Si(001) 2×1 surface at the same $h\nu$ of 17.6 eV at all the corresponding θ_{e} 's. An extensive comparison with such clean surface spectra confirms that $S_1 - S'_4$ cannot be assigned to any surface or bulk features of the clean Si(001) surface. It should also be noted that the features $S_1 - S'_4$ cannot be related to surface umklapp transitions of any bulk features around normal emission $(\overline{\Gamma}_{00})$ since all these states appear clearly at the SBZ point of J'_{11} . It is not clear whether or not the state S_5 (well inside the bulk band region) has a surface origin since a rather similar feature is observed on the clean surface. There are also a few other minor features in the bulk band region that are not considered.

Although most of the previous literature has referred to a DD 2×3 phase with characteristic streaks in its LEED pattern formed at annealing temperatures higher than ~ 300 °C, it was recently shown that a SD 2×3 phase without such streaks can be formed by proper preparation.⁶ This SD sur-



FIG. 4. Experimental dispersions for the DD Si(001)2×3-Ag surface along the [010] azimuth taken from the spectra shown in Fig. 3. The small and large symbols denote the rather distinctive and weak spectral features, respectively. The corresponding emission angles (θ_e) are also indicated by thin dashed lines. The thick dashed line is the edge of bulk bands projected into the 1×1 SBZ. The dispersions determined for the surface states are depicted by gray lines. The dashed parts of the gray lines indicate the ambiguous parts of the dispersions.

face is ideal for the investigation of surface-state dispersions along [110] and [110] axes. This is mainly due to the absence of the ambiguity from two coexisting domains of 2×3 and 3×2 . ARPES spectra for the SD 2×3 surface along the [110] azimuth are shown in Fig. 5. In this set of spectra, we can also find the two closely lying bands of S_1 and S_2 at BE's of ~0.9 and ~1.1 eV, respectively. S_3 occurs also at the same BE as along the [010] azimuth of the DD 2×3 surface (Figs. 3 and 4). At higher BE, S_5 is observed clearly with almost no dispersion.

Figure 6 shows the dispersions of the spectral features along the [110] azimuth. The dispersions of S_1 , S_2 , and S_3 are very similar to those of the corresponding bands of the DD 2×3 surface along [010]. S_5 peaks have relatively prominent intensities also in this azimuth. On the other hand, the sharply dispersing state from \overline{J}_{00} to \overline{J}_{10} (denoted by b' in the figure) is assigned as a bulk feature.¹⁶ ARPES spectra for the DD 2×3 surface measured along the [110] azimuth (not shown here) are essentially identical to those of the SD 2×3 phase shown in Fig. 5. This can be naturally explained from the identical surface structure of these two phases⁶ and the small dispersions of the major surface states along both [110] and [110] (shown below) axes.

Figure 7 shows the dispersions of the surface states of the SD 2×3 surface along the other major symmetric axis of [110]. The raw spectra for this azimuth are not shown here. One can identify the three low-BE surface states within the gap region, S_1 , S_2 , and S_3 , with similar dispersions to those along the [110] azimuth. At the SBZ part of $\overline{J}'_{01} - \overline{\Gamma}_{02}$, a dispersing band was observed at $E_B = 2.5 - 2.8$ eV. By com-



FIG. 5. Similar to Fig. 3, but for the SD Si $(001)2\times3$ -Ag surface along the [110] azimuth.

paring its BE at \overline{J}'_{01} to that of the equivalent SBZ point along [010], \overline{J}'_{11} , (see Fig. 4), this band is identified as S'_4 . The deep-lying surface resonance state S_5 is also observed with only a small dispersion. The dispersing band b'' at $\overline{\Gamma}_{01}$ - $\overline{\Gamma}_{02}$ is thought to be a bulk feature similar to b' in Fig. 6.

The surface-state nature of these bands along [110] and [110] is also checked through a careful and extensive comparison with clean surface spectra taken at the same condition as mentioned above. S_1 , S_2 , and S_3 cannot be assigned as surface umklapp features since there are no corresponding bulk features at the same binding energies and their intensities do not show any significant decrease at the second SBZ. It might be possible to relate S'_4 as a surface umklapp feature to a feature observed at a similar BE around normal emission.

To summarize the ARPES results, we have identified three clear surface states within the bulk band gap, S_1 , S_2 , and S_3 , whose dispersions are very small. In addition, surface states S_4 and S'_4 are observed with BE's of ~2.2 and ~2.6 eV, respectively, mainly in the deeper region of the bulk band gap around $\sim \overline{J}'_{11}$ along the [010] azimuth. In Figs. 3–7, it is shown that DD and SD 2×3 surfaces are semiconducting with a band gap larger than ~0.8 eV. No sign of spectral features at $E_B < 0.8$ eV was detected.



FIG. 6. Similar to Fig. 4, but for the spectra shown in Fig. 5, that is, for the ARPES spectra of the SD Si(001)2 \times 3-Ag surface along the [$\overline{110}$] azimuth.

IV. DISCUSSION

Clarifying the origin of surface states observed requires detailed information on the surface structure in advance, which is not available, as discussed below. However, it is tempting to relate S_1 and S_2 to the Si dangling bonds from their BE's. Two possibilities can be suggested: (i) the 2×3 unit cell itself has Si surface atoms with dangling bonds not saturated or (ii) these states are due to the bonds between Ag and Si which still have a strong dangling-bond character. As an example of the former case, one can find the danglingbond surface state of the Si(001)2 \times 3-In surface, which comes from the bare Si dimers intrinsic to the 2×3 -In unit cell.^{14,17} As examples of the latter case, one can mention alkali-metal-adsorbed18,19 and the group-III-metaladsorbed^{13,14,17,20} Si(001) surfaces. It should be noted that these low-BE states may also originate from the possible overlap between 5s valence electrons of Ag adsorbates.

As for the higher-BE bands of S_3 , S_4 , and S'_4 it can be suggested that they are due to the bonds between Ag 5s valence electrons and Si dangling bonds or due to the bonds between the Si dangling bonds through reconstruction of Si surface atoms. In fact, surface states similar to S_3 , S_4 , and S'_4 have been found at similar BE's on Si(001)2×2-Al (Ref. 20) [-In (Ref. 13)] and Si(001)2×3-In (Ref. 14) surfaces, which were assigned as being due to the bonds between the metals and Si dangling bonds. The Ag 4d band origin for these surface states is not pluasible since their BE's are well above the Ag 4d BE. Any further attempt to understand origins of the surface-state bands observed in the present work is hindered by the lack of proper surface structure information.

As for the structure of the 2×3-Ag surface, there have been two available models up to now. One is a simple structure model with Ag adsorbates between the intact Si dimers.⁵ The coverage of Ag in this model is $\frac{1}{3}$ ML. This structure is



FIG. 7. Similar to Fig. 4, but for the ARPES spectra of the SD $Si(001)2\times3$ -Ag surface along the [110] azimuth, which are not shown in this paper.

very close to those of the alkali-metal-adsorbed 2×3 phases on the Si(001) surface.²¹ This $\frac{1}{3}$ -ML model, however, is inconsistent with the present result since the possibility of preserved Si dimers can be ruled out clearly; a comparison of the present results with clean surface spectra reveals that all the surface states related to the Si dimers of the clean surface (such as A, B, D, I, H, and G in Ref. 16) are found to disappear on the 2×3 -Ag surface as shown, in part, in Fig. 2(b). That is, the surface reconstruction of the 2×3 -Ag phase is not based on Si dimers. This is in sharp contrast to Si(001)2×2-In,¹³ $Si(001)2 \times 2-Al$,²⁰ cases of the $Si(001)2\times 3\text{-In},^{14}$ and $Si(001)2\times 3\text{-Cs}$ (Ref. 22) surfaces where some of the surface states related to Si dimers have been clearly identified due to the Si dimers preserved beneath the adsorbates. The $\frac{1}{3}$ -ML model is also inconsistent with most of the recent investigations, which reported the Ag coverage of the 2×3 phase as $\ge \frac{1}{2}$ ML.⁴⁻⁷ It should also be noted that the recent STM image showing a lack of mirror symmetry along the $[\overline{1}10]$ axis⁴ cannot be explained by this simple model.

The other available structure model was proposed by Michley *et al.*,⁷ which has a Ag coverage of $\frac{1}{2}$ ML, and a topmost layer mixed with Ag and Si. This mixed layer model and all other possible structure models based on the $\frac{1}{2}$ -ML coverage (three Ag atoms within a 2×3 unit cell) have an odd number of electrons in the 2×3 surface unit cell: twelve (six) *sp* electrons of Si dangling bonds with dimer bonds broken (preserved) and three *s* electrons are neglected since they are well isolated from the BE range we consider. Yet even taking into account Ag 4*d* electrons at $\frac{1}{2}$ ML.

An odd number of electrons in a unit cell leads to a metallic surface, in apparent contradiction with the present result, showing a clear and large band gap. The only way to avoid this contradiction is to resort to a strong electron correlation, which might lead to a Mott-Hurbard-type insulating state. Such electron correlation effects have been discussed in few cases of alkali-metal adsorptions on semiconductor surfaces.²³ However, we think that one should suspect the structure model before any serious consideration of the very rare case of a strong electron correlation on a semiconductor surface. One strong reason to suspect the $\frac{1}{2}$ -ML structure model comes from a recent x-ray photoelectron spectroscopy (XPS) and LEED investigation reporting a nominal coverage of the 2×3 -Ag surface of 0.6 ML or larger.⁶ This was also the case for our own calibration of the Ag coverage for the best 2×3 LEED pattern. It is also worthwhile to note that any efforts to theoretically simulate the measured photoelectron diffraction patters of the 2×3 phase by the $\frac{1}{2}$ -ML structure models was unsuccessful.²⁴ A Ag coverage of $\frac{2}{3}$ ML (four Ag atoms in a 2×3 unit cell), instead of $\frac{1}{2}$ ML, is consistent with these reports. This leads to an even number of surface electrons and naturally to a semiconducting surface. Thus a structure model based on a Ag coverage of $\frac{2}{3}$ ML is strongly favored by the present result. Of course a very careful measurement of the Ag coverage using the probes such as ion scattering can be very helpful in solving this problem. We leave as a task for future research the refinement of a structure model with $\frac{2}{3}$ -ML Ag adsorbates and without Si dimers.

V. CONCLUSIONS

An ARPES study has been performed to investigate the electronic structures of single- and double-domain $Si(001)2 \times 3$ -Ag surfaces. Through detailed ARPES measurements using synchrotron radiation for different SBZ lines, we have identified the presence and dispersions of five different surface state bands S_1 , S_2 , S_3 , S_4 , and S'_4 within the bulk band gap (0.8-3.5 eV in BE). All surface states related to the Si surface dimers disappear upon forming the 2×3-Ag phase, indicating that all Si dimers are broken. This observation denvs the simple $\frac{1}{3}$ ML structure model proposed by Winau *et al.*⁵ It is apparently shown that this surface is semiconducting with no spectral features between E_F and ~ 0.8 eV in BE. This result contradicts the recently proposed structure model based on an Ag coverage of $\frac{1}{2}$ ML (Ref. 7) through simple electron counting. From this and a recent XPS/LEED result,⁶ it is suggested that the nominal coverage of the 2×3 phase could be $\frac{2}{3}$ ML with four Ag atoms in a 2×3 unit cell. Further detailed surface structure studies on this surface phase are required. The present investigation provides the experimental surface-state dispersions, which can play an important role in determining the surface structure of the 2×3 -Ag surface if a proper theoretical calculation is available.

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