STM observation of the Si(111)-c(12×2)-Ag surface

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The Si(111)-c(12×2)-Ag surface phase was observed by scanning tunneling microscopy (STM) at 65 K and its atomic structure was analyzed in detail. The phase is the ground-state structure within the framework of ‘Honeycomb-Chain Channel’ reconstruction, attained through successive phase transitions by cooling from 3×1 (≥ ca. 500 K) and 6×1 phases (≥ ca. 100 K). The transitions are likely order-disorder types with two-step freezing of fluctuation of the Ag atom positions. [DOI: 10.1380/ejssnt.2005.151]

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I. INTRODUCTION

Noble metals, especially Ag adsorptions on Si surfaces have been at the center of efforts in surface science to understand the fundamental physical properties of metal/semiconductor interfaces during the past decades [1–7]. This is mainly due to a minimal chemical interaction between Ag and Si (compared with Au or Cu) and due to formation of the well-defined interface structures.

On the Si(111) surface, two surface superstructures, √3×√3 and 3×1, are well known to appear at the Ag coverage of one monolayer (ML) and 1/3 ML, respectively [3–5]. These surfaces have been model systems to develop surface science techniques and almost all the methods have been used to determine their atomic/electronic structures [8–10]. The ground state of the Si(111)-√3×√3-Ag surface has now been widely accepted to possess a so-called “InEquivalent Triangle (IET)” structure [11, 12], while the structure of the Si(111)-3×1-Ag is well described by the “Honeycomb Chain Channel (HCC)” model [13]. Furthermore, these surfaces have been found to undergo various phase transitions with temperature [11–15] and the systems have now become important playgrounds to study exotic low-dimensional phase transitions on solid surfaces [16–19]. For example, the √3×√3-Ag surface exhibits an empty-state STM image of a hexagonal-lattice pattern at low temperature but a honeycomb-lattice one at room temperature [11, 12]. The transition has now been vigorously argued whether it is an order-disorder type or a disclaptic type [8, 9, 20, 21]. On the other hand, the 3×1-Ag phase transforms to 6×1 below 500 K and subsequently to c(12×2) below 100 K [10]. The transition mechanism has also been controversial. The 3×1-to-6×1 transition is proposed to be associated with configuration change of the Si-Ag-Si bonds [13, 15] and it is also induced by STM tips at room temperature [22, 23]. The recent photoemission spectroscopy study has reported little change in the Si2p core levels during the 6×1-to-c(12×2) transformation, and has proposed that the transition is the order-disorder type [14].

In the present study, we have performed detailed STM observations of the Ag/Si(111) superstructure, covered by 1/3 ML of Ag, at ~65 K. While the surface has the 3×1 and 6×1 periodicities above and below 500 K, respectively, it shows a long-range ordered phase of c(12×2) at ~65 K. Through a comparison with the present STM results and simulations on the 3×1 and 6×1 structures previously reported, a possible atomic structure model for the c(12×2) phase has been obtained. The nature of the 3×1-to-6×1-to-c(12×2) phase transition is fairly described by position fluctuations of Ag atoms within the framework of the HCC model [13, 15]. The two-step transition seems to be the order-disorder type associated with two different types of the Ag adsorption sites.

II. EXPERIMENTS

The experiments were carried out using a commercial ultrahigh-vacuum (UHV) low-temperature STM-RHEED (reflection-high-energy electron diffraction) system (UNISOKU USM501 type) [12, 16]. The sample crystals were cut from an n-type Si(111) wafer (P-doped, 1×1).

FIG. 1: (a) An empty-state STM image taken with tip bias of -2.0 V and tunneling current of 0.3 nA in constant-height mode. The c(12×2) unit cell is indicated by a red parallelogram. (b) A Fourier transformed pattern of (a). (c) A schematic LEED pattern of a triple-domain c(12×2) surface superstructure. The fundamental spots are painted black. Green spots are the 6×1 fractional-order spots, and red ones are the c(12×2) spots.
2 \sim 15\Omega \text{cm}. A clean Si(111)-7 \times 7 surface was prepared by a cycle of in situ resistive heat treatments. The $\sqrt{3} \times \sqrt{3}$-Ag surface was first made by monolayer Ag deposition at the substrate temperature of $\sim 520^\circ\text{C}$. A monolayer, 1 ML, corresponds to $7.83 \times 10^{14}$ atoms/cm$^2$, the number density of Si atoms in the topmost layer of the (111) face. Silver was evaporated from an alumina-coated W basket, and the coverage was estimated by simultaneous observation of RHEED during the constant-rate deposition, showing a complete conversion of the surface structure from the $\sqrt{3} \times \sqrt{3}$ to the $\times 2$ at 1 ML coverage. A Si(111)-3 $\times$ 1 -Ag surface was made by desorbing Ag from the Si(111)-$\sqrt{3} \times \sqrt{3}$ -Ag surface by annealing at $T > 600^\circ\text{C}$ [4], and it changed into the $6 \times 1$-Ag by cooling it below $\sim 200^\circ\text{C}$. When the sample was cooled down further below room temperature, it changed into the c(12$\times$2)-Ag phase. The STM observation was done at $\sim 65$ K. During the present STM experiments, the pressure was kept below $1 \times 10^{-10}$ Torr.

III. RESULTS AND DISCUSSION

Figure 1 (a) displays a typical empty-state STM image taken at $\sim 65$ K. The results show two-orientational domains of the long-range ordered c(12$\times$2) phase separated by a surface step. The domains have stripe patterns rotated by 120$^\circ$ to each other. In order to find the relation between the present STM image and the previously reported low-energy electron diffraction (LEED) pattern [14], we have performed Fourier transform (FT) of the STM image. The FT pattern of (a) is presented in Fig. 1 (b). In addition to fundamental spots labeled (10) and marked by white circles, one can identify fine spots which are originated from the superstructure in the double-domains in Fig. 1 (a). For comparison, a sketch of a LEED pattern from the triple-domain c(12$\times$2) surface [14] is given in Fig. 1 (c). The FT pattern (b) reproduces the LEED pattern well, especially one can find fractional-order spots corresponding to red spots in (c), which indicate the c(12$\times$2) superstructure. This is the first confirmation of the phase by STM.

The appearance of the c(12$\times$2)-Ag structure in STM images has strong dependence on the bias voltage polarity, which is similar to those of the $6 \times 1$-Ag and the $3 \times 1$-Ag structures [22, 24–26]. Figure 2 show portions of dual-bias STM images taken at -2.0 V (a) and 2.0 V (b) tip biases, respectively. The c(12$\times$2) unit cells are indicated in both empty- and filled-state images and placed on equivalent position of the surface. Bright stripes are spaced by 3a apart from each other in both images (a) is the size of 1 $\times$ 1 unit cell, $a = a_o/\sqrt{3} = 3.84\AA$). One can find some differences between (a) and (b). First, the contrast is reversed between the empty- and filled-state images; the bright stripes in (b) correspond to the dark trenches in (a). This feature is the same as STM images of the $3 \times 1$-Ag (6 $\times$ 1-Ag) structure. Second, in the empty-state images (a), every row consists of bright protrusions spaced by 2a along it. This is characteristic to the c(12$\times$2) phase. On the other hand, rows in the filled-state images (b) show stripes without clear 2a-periodicity modulation along them.

Figures 3 (a) and (b) display empty-state images taken at tip bias of -1.2 V and -1.0 V, respectively. In Fig. 3 (a), the bright features with 2a spacing are identified in every row more clearly than in Fig. 2(a). With a close look, small subsidiary protrusions, marked by green circles, are found nearby the main bright protrusions. Furthermore, one can recognize in Fig. 3(b) that the main bright features look different between adjacent rows; they look oval in a row but rectangle in the next rows, as illustrated by red in (b). They have the same shape within each row. This alternate arrangement of different features in the main protrusions makes a six-times super-periodicity across the stripes. Furthermore, they are arranged in out-of-phase between the neighboring rows, which make a 12-times super-periodicity across the rows. Thus, it is now obvious that the c(12$\times$2) periodicity is resulted from such an out-of-phase arrangement of the two kinds of main protrusions with different shapes across the stripes, which, on one hand, have the 2a periodicity along the stripes.

Next we discuss the relation between the STM images and the atomic structure. As described above, the c(12$\times$2)-Ag phase undergoes transitions to the $6 \times 1$-Ag above $\sim 100$ K and subsequently to the $3 \times 1$-Ag above 500 K [10]. Contrary to only one paper on the c(12$\times$2)-Ag [14], there has been a considerable number of studies devoted to structure determination of the $6 \times 1$-Ag and $3 \times 1$-Ag phases. In the following discussion, we argue the
c(12×2)-Ag atomic structure based on those of the 6×1-Ag and 3×1-Ag phases because the STM images can be understood by some modulations of those of the 3×1/6×1 structures. Through various structure models proposed so far for these two phases [13, 15, 22, 24, 25], the HCC model is most widely accepted [13], which is illustrated in Fig. 4(a). The electronic and structural properties based on this model have shown complete agreements with experimental data of 3×1 phases induced by alkali metals as well as Ag adsorptions on Si(111) [13, 15, 27, 28]. According to theoretical simulations [13, 28], the adsorbed metal atoms and p_z orbitals of inner Si atoms (labeled by A-D in Fig. 4(a)) appear bright in the empty-state images with tip bias of ~1.5 V. The protrusions in the filled-state images, on the other hand, come from the outer Si atoms (atoms 1-4 in Fig. 4(a)), making chemical bonds with Ag atoms) as well as the inner Si atoms in the Si honeycomb chains. This is consistent to broad stripes observed in Fig. 2(b). These Si atoms have three occupied surface states as revealed by angle-resolved photoemission spectroscopy (ARPES) measurements [14, 26]. Thus, the empty-state images show bright stripes centered on the Ag rows, while the bright stripes are on the Si honeycomb chains in the filled-state images, exhibiting contrast reversal by bias-polarity change.

There is, however, a slight difference between the alkali-metal- and Ag-induced 3×1 structures. In the case of alkali metals, the metal atoms sit on the T1 sites [13, 27, 28], as indicated in Fig. 4(a). Its structure model is presented in Fig. 4(b). On the other hand, the adsorption site of Ag atoms in the 3×1-Ag is proposed to slightly shift from the T1 site, as labeled by β_1 and β_2 in Fig. 4(a), occupying asymmetric locations [10, 13–15]. The model is schematically given in Fig. 4(c). It is worth noting a distinction in the coordinations between the alkali-metal and Ag atoms. The alkali-metal atoms have purely electrostatic interactions with Si atoms, favoring a three-fold coordination, while Ag atoms form weak Ag-Si bonds which are more covalent-bond like, favoring a two-fold coordination [10, 13]. Since the reconstructed Si layer in the 3×1-HCC model has a mirror plane parallel to the [11 0] direction (perpendicular to the rows), there are two possible Ag-Si bondings, Si(2)-Ag(β_1)-Si(1) (Ag is on the β_1) and Si(3)-Ag(β_2)-Si(1) (Ag is on the β_2) as shown in Fig. 4(a). By making the Si-Ag-Si bond configurations different between the adjacent rows alternately, the six-times super-periodicity across the rows is formed as shown in Fig. 4(d). Conversely, the 3×1 structure above ~500 K is a time-average structure of the fluctuating 6×1 structure where Ag atoms randomly fluctuate between β_1 and β_2 sites. Therefore, the transition between the 3×1 and 6×1 is believed to be an order-disorder type [10, 13, 15]. Since, on the other hand, the alkali-metal atoms sit on the symmetric T1 site, a 6×1 structure cannot exist in the case of alkali-metal-induced 3×1.

In order to make assignments of the features observed in the STM images for the c(12×2)-Ag phase, a theoretical calculation based on a proper structure model is essentially required, which is, however, not yet available. Therefore, it is tempting to relate the present STM im-

FIG. 4: Schematic illustrations of various structure models of the Ag/Si(111) systems. Silicon atoms at the top most layer and at an upper (lower) part of the subsurface Si double layer are colored light gray and dark gray (black), respectively. (a) The HCC model [13] of Si reconstruction. Silicon atoms and adsorption sites described in the text are labeled differently. (b) Structure model of the alkali-metal (orange) induced 3×1 phase. (c–e) Silver(purple)-induced superstructure of the (c) 3×1, (d) 6×1, and (e) c(12×2) phases with each unit cell(red). Features of the empty-state STM images (Fig. 3) are overlapped in (e).
FIG. 5: Schematic illustrations of a potential (φ) curve for the two-step order-disorder phase transition with respect to two normal coordinates. The qy coordinate corresponds to Ag fluctuation perpendicular to the surface (with associated Si motions) responsible to the 6×1-to-c(12×2) phase transition, while qz indicates changes in the Si-Ag-Si bonding configurations (in-plane Ag fluctuation), responsible to the 3×1-to-6×1 transition.

ages to the structure models of the 3×1-Ag [Fig. 4(c)] and 6×1-Ag [Fig. 4(d)] surfaces. Since, as described above, the Ag atoms and pz orbitals of the inner Si atoms appear bright in the empty-state images, the oval and rectangular maxima indicated in Fig. 3(b) are fairly assigned to Ag atoms, while the circular subsidiary protrusions in Fig. 3(a) are the inner Si atoms. In Fig. 4(e), the STM features in Fig. 3 are overlapped on the structure model of the 6×1-Ag [Fig. 4(d)]. The positions of the main protrusions (oval and rectangular shapes) and circular subsidiary protrusions in the STM images obviously coincide with the locations of Ag and Si atoms, respectively. But only the every second Ag atoms along the rows correspond to the protrusions. This indicates non-equivalent positions/electronic states of Ag atoms alternately along the row. We tentatively attribute this upward and downward shifts of Ag atoms normal to the surface alternately along the Ag rows; only the Ag atoms shifting towards vacuum becomes brighter in the empty-state images. There can be, however, other explanations for the double-periodicity main protrusions in the Ag rows in the 6×1-Ag phase. While the large barrier along coordinate y indicates changes in the Si-Ag-Si bonding configuration, Si(1)-Ag-Si(2) and Si(1)-Ag-Si(3) maxima indicated in Fig. 3(b) are fairly assigned to Ag atoms between the up and down positions, the 6×1 is a time-averaged structure of the fluctuating c(12×2) phase. In other words, the 6×1-to-c(12×2) phase transition is a kind of order-disorder one caused by freezing the fluctuation of Ag atom positions.

Therefore, the 3×1-to-6×1-to-c(12×2) phase transitions seem to be originated from the position fluctuations of Ag atoms in the HCC model. Though the conclusive characterization of the present transition requires further studies such as detailed STM simulations including time averaging [20, 21], the previous reports on the electronic structure have suggested the transitions are the order-disorder types [10, 14]. Here, we make a brief summary of a nature of the 3×1-to-6×1-to-c(12×2) phase transitions based on the disordering of Ag atom positions. Figure 5 illustrates a potential surface for the two-step order-disorder phase transitions with two axes of the normal coordinates, qy and qz. The coordinate qy corresponds to the fluctuation of Ag atoms parallel to the surface (between β′ and β′′ sites), and qz corresponds to the fluctuation of Ag atoms normal to the surface at both of β′ and β′′ sites. The potential surface is composed of two different types of potential barriers, a large one along qy and small ones along qz. This results in formations of four minima corresponding to four kinds of Ag atom positions in the c(12×2) phase; two different Ag heights (up and down) at both of β′ and β′′ sites, as shown in Figs. 5 and 4(d). The small potential barrier between the two minima along qy axis is responsible for the c(12×2)-to-6×1 transition, while the large barrier along qz corresponds to a change of bonding configuration, Si(1)-Ag-Si(2) and Si(1)-Ag-Si(3) in Fig. 4(c), governing the 6×1-to-3×1 transition. The difference in the barrier heights corresponds to different transition temperatures.
IV. CONCLUSION

We have investigated the structure of the long-range ordered phase of c(12×2) on Si(111) covered by 1/3 ML of Ag, by means of STM at ~ 65 K. Through a comparison with the previous STM results and simulations on the Si(111)-3×1-Ag and -6×1-Ag structures, a possible structure model for the c(12×2) phase has been obtained. The nature of the 3×1-to-6×1-to-c(12×2) phase transition is fairly described by fluctuation of Ag atoms within the framework of the HCC model [13, 15]. We propose that the in-plane fluctuation of Ag atoms, which is associated with the periodicity doubling across the chains by inter-chain interaction, is responsible for the 3×1-to-6×1 phase transition, while the out-of-plane fluctuation of Ag atoms, which causes the periodicity doubling along the chains by intra-chain interaction, is important for the 6×1-to-c(12×2) transition. These two order-disorder phase transitions occur at different temperatures due to different heights of potential barriers between the equivalent stable atomic configurations.

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