Successive Phase Transitions Induced by Ca and Sr Adsorptions on a Si(111) Surface

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(Received 7 June 2004; Accepted 24 June 2004; Published 30 June 2004)

Surface superstructures induced by adsorptions of divalent atoms (Ca and Sr) on a Si(111) substrate were investigated by reflection-high-energy electron diffraction (RHEED). After depositing Ca or Sr of 1~3 monolayers, followed by post heating at temperatures ranging from 400 °C to 900 °C, successive changes in structure were observed due to the coverage decrease by thermal desorption of the adsorbates; 1 \times 1, \sqrt{3} \times \sqrt{3}, 2 \times 1, 9 \times 1, 7 \times 1, 5 \times 1, 3 \times 1, and also complicated undefined superstructures were observed before returning to the clean 7 \times 7 structure. While the observed changes were similar to each other between the Ca and Sr cases, there were differences. The 9 \times 1 phase was clear for Sr adsorption, while the 7 \times 1 was distinct for Ca case. For the Sr case, the superlattice spots of the adjacent phases were coexisted at the intermediate coverages, meaning that the domain of the two phases coexisted separately (phase separation). For Ca case, on the other hand, the superlattice spots continuously shifted in position to those of the next phase with decrease of Ca coverage. This phenomenon was well reproduced by a simple kinematical simulation of diffraction. For example, when the 5 \times 1 and 3 \times 1 superstructures are mixed microscopically with different ratios, a new superlattice spot appears between the fifth- and third-fractional order spots, and its position shifts depending on the area ratio. Such a microscopic phase mixture is consistent with the previous observations by scanning tunneling microscopy.

[DOI: 10.1380/ejssnt.2004.178]

Keywords: Divalent atoms; Surface Superstructures; Phase Transitions; Two-Phase Coexistence; Reflection high-energy electron diffraction (RHEED); Silicon; Calcium; Strontium

I. INTRODUCTION

It is well known by a huge number of studies that monovalent atoms (alkali metals and Ag) adsorption on a Si(111) surface commonly induces a 3 \times 1 surface superstructure with 1/3 monolayer (ML) coverage [1~4], and its atomic arrangement is solved by a so-called honeycomb chain (HCC) model [5~7]. For adsorption of divalent metal atoms such as alkaline-earth metals (AEM; Mg, Ca [8~11], Sr, and Ba [12, 13]) and rare-earth metals (Yb and Sm) [14~21], on the other hand, similar 3 \times 1 structures are induced, too, but they are accompanied by half-order streaks in electron diffraction patterns, showing 3 \times 2' structures. Since it turns out that the Ba coverage is 1/6 ML for the 3 \times 2' phase [13], it is believed that the coverage of other divalent atoms is also 1/6 ML. This reasonably explain semiconducting nature of the 3 \times 2' phases by the electron counting rule.

Another interesting point for the divalent atom adsorption on Si(111) surface is that, in addition to the 3 \times 1 phase (here we call the 3 \times 2' by 3 \times 1 for simplicity), n \times 1 structures with n =2, (3), 5, 7, 9, \ldots are formed by coverage increase, which is not observed for the monovalent atom adsorptions. These n \times 1 phases show stripe structures in scanning tunneling microscope (STM) images, showing highly anisotropic characters in atomic and electronic structures. It is proposed for the atomic structure that the n \times 1 phase is composed of two kinds of structural units, the HCC structure (that is for the 3 \times 1 reconstruction) and a so-called Seiwatz chain structure (that has a 2 \times 1 reconstructed structure) [8, 17]. In the 2 \times 1 model for the highest Ca coverage (1/2 ML), Ca atoms are located between \pi-bonded chains formed by five-membered Si atoms. This Si chain is called a Seiwatz chain [22]. For example, the 5 \times 1 structure consists of an alternate array of the HCC and Seiwatz Si chains, and the 7 \times 1 is composed of a periodic array of a HCC and two Seiwatz chains. Depending on the ratio between the HCC and Seiwatz chains, n \times 1 superstructures with different n are formed. The Seiwatz chain is unstable and never formed by monovalent atom adsorptions, but it becomes as stable as the HCC chains by divalent atom adsorptions.

Most of the previous studies on Ca and Sr adsorptions on Si surfaces in early days were carried out by depositing CaF₂ and SrF₂ [11, 23~26]; it is only recent that deposition of metal Ca itself is used [8, 9, 17, 27, 28]. By heating the surfaces up to 700~800 °C after depositing CaF₂, fluorine atoms preferentially desorb from the substrate, leaving Ca atoms only on the surfaces [7]. A 3 \times 1 phase with Ca was thus found selectively along step edges on a Si(111) surface [29, 30]. A difference between SrF₂ and CaF₂ adsorptions on Si(111) surfaces is discussed in Ref.[31]. SrF₂ adsorption on a Si(100) surface was also studied by scanning tunneling microscopy (STM) [32]. There are reports on Si(111) surfaces adsorbed by other divalent atoms such as Mg [21], Ba [18], Sm [20, 21], and Yb [20, 21]. While systematic studies with adsorption of Ca are reported, there no report for adsorption of Sr itself.

We report here systematic observations of continuous changes in surface structures induced by Ca and Sr adsorptions on a Si(111) substrate using reflection-high-energy electron diffraction (RHEED). Since we employed a stepwise post-annealing method after room-temperature depositions, fine features during the structural transitions could be investigated. We found similarity as a whole in structural changes induced by coverage changes between the two elements, though with some differences between them. An interesting point is

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FIG. 1: RHEED patterns from the Ca-adsorbed ((a)-(e)) and Sr-adsorbed ((f)-(j)) Si(111) surfaces. By high-temperature annealing, the metal coverage decreased, giving rise of successive structural changes for both cases to reach the $2 \times 1$ phases. The annealing temperature was (a) 540°C, (b) 560°C (an undefined superstructure A), (c) 580°C ($\sqrt{3} \times \sqrt{3} + 2 \times 1$ + undefined structure A), (d) 600°C ($\sqrt{3} \times \sqrt{3} + 2 \times 1$), and (e) 620°C (dominated by $2 \times 1$), respectively, for Ca case, and (f) 350°C, (g) 420°C ($\sqrt{3} \times \sqrt{3}$), (h) 540°C ($\sqrt{3} \times \sqrt{3} + 2 \times 1$), (i) 560°C, and (j) 600°C ($2 \times 1$ + undefined structure B), respectively, for Sr case.

that structural transitions from the $2 \times 1$ to the $3 \times 1$ via different $n \times 1$ phases proceed in different ways between Ca and Sr cases; a phase separation between the two neighboring phases was observed for Sr case, while the Ca-adsorbed surfaces showed a microscopic mixture of the two structures at the intermediate coverages, which produced diffraction spots between those of the two phases. These phenomena was well reproduced by a kinematical diffraction simulation.

II. EXPERIMENTAL PROCEDURES

Powder of Ca with 99.2 % purity was installed into a K-cell, and it was thoroughly degassed in vacuum. Calcium began to evaporate around 400 °C. The pressure was kept at $(3 \sim 6) \times 10^{-9}$ Torr during evaporation. On the other hand, it was difficult to prepare Sr for evaporation, because shots of Sr were kept in oil to prevent oxidation, so that the oil was washed away by ethanol in a supersonic bath. The shots was swiftly introduced into vacuum.
FIG. 2: RHEED patterns from the Ca-adsorbed (right column) and Sr-adsorbed (left column) Si(111) surfaces. By high-temperature annealing, the coverage of metals decreased, giving rise of successive structural changes for both cases from the $2 \times 1$ (1/2 ML) to $3 \times 1$ (1/6 ML).

After prolonged degassing thoroughly at evaporation temperature of 300 °C in vacuum, the pressure was kept in the range of $10^{-9}$ Torr during deposition. Depositions of precise amounts were done by computer-controlled shutters in front of the evaporators with constant K-cell temperatures, with aid of a quartz thickness monitor. A $p$-type Si(111) wafer was used, having $30 \times 4 \times 0.3$ mm$^3$ in size and a resistivity of $100 \sim 150$ Ωcm at room temperature. The heating temperature of the wafer was measured with an optical pyrometer.

A few monolayers of Ca or Sr were deposited onto the clean Si(111)-7×7 surface at room temperature, and then the sample was annealed at fixed temperatures until the structure changes have completed at each temperature. The annealing temperature was raised stepwise. The RHEED pattern was observed and recorded after cooling the sample down to room temperature after each annealing process. Since Ca and Sr gradually desorbed from the surface by the annealing, the observed structural changes were due to the coverage decrease.
III. RESULTS

A. Before formation of $2 \times 1$ phases

By depositing two monolayers of Ca on the $7 \times 7$ clean surface at room temperature, the $7 \times 7$-superlattice spots disappeared completely. By annealing the sample around 540°C, the RHEED pattern shows streaky reflections as shown in Fig. 1(a). Around 560°C, a complicated pattern appears (Fig. 1(b)), whose periodicity is not yet determined. Around 580°C, $\sqrt{3} \times \sqrt{3}$ spots coexist (Fig. 1(c)). Around 600°C, the undefined superstructure disappears, instead 2 × 1 spots appear coexisting with the $\sqrt{3} \times \sqrt{3}$ spots (Fig. 1(d)). Around 620°C, the $\sqrt{3} \times \sqrt{3}$ spots are weakened and the 2 × 1 spots dominate (Fig. 1(e)). Finally a single phase of 2 × 1 with triple orientation domains is formed around 620–680 °C (Fig. 2(a), right half).

As in the case of Ca deposition, two monolayer of Sr deposition on the $7 \times 7$ clean surface diminishes the $7 \times 7$-superspots. Figure 1(f) is a pattern after 350 °C annealing, showing almost no super-reflections appearing. Around 420°C, a single phase of $\sqrt{3} \times \sqrt{3}$ structure appears (Fig. 1(g)). Around 540°C, 2 × 1 spots coexist and increase the intensity (Figs. 1(h)(i)). Around 600°C the $\sqrt{3} \times \sqrt{3}$ spots disappear, instead complicated super-reflections appear and coexist with the 2 × 1 phase (Fig. 1(j)). Finally a single phase of the 2 × 1 structure is obtained at 630°C (Fig. 2(a), left half).

The above-mentioned structural changes up to 650 °C annealing for Ca and Sr depositions are summarized in Fig. 3. Before reaching the 2 × 1 structure, $\sqrt{3} \times \sqrt{3}$ phases are commonly observed. The metal coverage should be decreased by higher temperature annealing due to desorption. Since the Ca saturation coverage of the 2 × 1-Ca phase is 1/2 ML [8], metal coverage for the $\sqrt{3} \times \sqrt{3}$ phase should be 2/3 ML or 1ML. The undefined structures having complicated reflections are also observed for both metal adsorbates, but at different annealing temperatures.

B. After formation of the $2 \times 1$ phases

After the 2 × 1 phase (1/2 ML) formed, a series of $n \times 1$ structures appear successively with decrease of metal coverage by higher-temperature annealing, and finally we reach a 3 × 1 phase (1/6 ML).

By prolonged annealing at 690 °C, the 2 × 1-Ca spots become streaky (Figs. 2(b)(c), right halves), and split into several super-spots (Figs. 2(d)(e)). Then the surface reaches a 7 × 1 pattern (Fig. 2(f)). By annealing 700 °C, the 7 × 1 spots become longer and shift to the positions of 5 × 1 spots (Fig. 2(g)), which is kept at 700–730 °C. At 730–760 °C, the 5 × 1 spots are elongated (Fig. 2(h)), and shift their positions (Fig. 2(i)) to 3 × 1 superspots (Fig. 2(j)). The 3 × 1 structure is kept at 760–790 °C. Around 800–850 °C, the 7 × 7 spots emerge and coexist with the 3 × 1 spots. Above 850 °C, the surface completely returns to the 7 × 7 clean structure. The changes are summarized in Fig. 3(a).

The details in change of superspots from the 2 × 1-Ca to the 3 × 1-Ca is clearly seen in Fig. 4(a) where corresponding parts in a series of RHEED patterns are displayed in a successive way. The fractional-order spots look continuously shift the positions. During this continuous change, we can recognize the superstructures of 7 × 1 and 5 × 1 only, while a streaky 9 × 1 phase may exist between the 2 × 1 and 7 × 1 phases.

For Sr case, a similar series of successive changes are observed from the 2 × 1 to 3 × 1 phases as shown in the left halves in Fig. 2. But the details in change of superspots are slightly different from the Ca case. Around 700 °C, the 2 × 1 spots become streaky (Fig. 2(b)), and split into several spots (Fig. 2(c)), which may correspond to a 11 × 1 structure. It changes further (Fig. 2(d)) and become a 9 × 1 structure (Fig. 2(e)). Around 720 °C, the 9 × 1 structure changes into a 5 × 1 (Fig. 2(g)) via a streaky 7 × 1 pattern (Fig. 2(f)). Around 730 °C, the 3 × 1 spots appear and coexist with the 5 × 1 (Fig. 2(h)), and gradually gain the intensity at the cost of the 5 × 1 intensity (Fig. 2(i)). Finally, the 5 × 1 spots disappear completely and a single phase of triple-domain 3 × 1 structure is obtained (Fig. 2(j)). These structural changes are summarized in Fig. 3(b).

The details in change of superspots are seen in Fig. 4(b), and can be compared with the Ca case. At the intermediate region, two kinds of superspots of the neighboring superstructures coexist for the Sr case, while the superspots shift their positions continuously for the Ca case at the intermediate region. The Sr case is easily understood in terms of two-phase coexistence where domains of two kinds of superstructures are separated at the intermediate coverages, so that the diffraction spots from them are simultaneously observed. However, it is not straightforward to understand the continuous shift of spot position observed in the Ca case. We have performed a kinematical simulation of diffraction to understand it in the next section.
FIG. 4: A series of a part in the RHEED pattern for (a) Ca- and (b) Sr-covered Si(111) surfaces, showing the changes in position of diffraction spots from the $2 \times 1$ (left side) to $3 \times 1$ (right side) phases.

IV. DISCUSSION

To understand the observed variation of electron diffraction spots during the $2 \times 1$ to $3 \times 1$ transitions, we have performed a simple simulation with the kinematical theory. We focus here the transition from the $5 \times 1$ to $3 \times 1$ structures only, and other transitions between different $n \times 1$ structures are understood similarly. We first prepare a one-dimensional lattice with a lattice constant $a$ (which is that of the unreconstructed $1 \times 1$-unit for Si(111), $a = 3.8 \, \text{Å}$). The number of lattice is set to be 80 because the length $80a$ is roughly equal to the coherent length of RHEED beam. The three-fold ($3 \times 1$) and five-fold ($5 \times 1$) superstructures are introduced by placing scatterers on the corresponding lattice points $r$:

$$r = n \cdot (3a) + m \cdot (5a), \quad n, m = 0, 1, 2, ... \quad (1)$$

The scattering amplitude $f(\mathbf{g})$ for a scattering vector $\mathbf{g}$ (or wavenumber in one dimension) is given by

$$f(\mathbf{g}) = \sum f_0 \exp(-2\pi i \mathbf{g} \cdot \mathbf{r}), \quad (2)$$

by assuming all scatters to be the same having the scattering factor $f_0$. The diffraction intensity $I$ at a point specified by $g$ in the reciprocal space is given by

$$I(g) = |f(g)|^2. \quad (3)$$

Figure 5 shows the calculated diffraction patterns with various configurations of the three-fold and five-fold superstructures. The large intensity spots at wavenumber of 0 and 0.26 Å$^{-1}$ correspond to the fundamental spots. In each arrangement, the same numbers of three-fold and five-fold structures are prepared. The alternate arrangement of the three- and five-fold unit cells, Fig. 5(a), results in an eight-fold superlattice periodicity and the simulation shows the appearance of eight-fold superspots, Fig.
FIG. 5: Arrangements of the three-fold and five-fold super-structures and their simulated electron diffraction patterns. (a,b) An alternate arrangement (eight-fold periodicity). (c,d) A random arrangement. (e,f) A condensed arrangement showing a phase separation. In the simulation, both numbers of the three-fold and five-fold structures are set to ten. The strong intensity spots at wave numbers of 0 and $\sim 0.26 \, \text{Å}^{-1}$ correspond to the fundamental "$1 \times 1$" points. Periodicities are indicated in the figure.

5(b). The intensity variation among the fractional-order spots is due to the finite size effect through the structure factor of our model. For the random arrangement of the three- and five-fold super-cells, Fig. 5(c), two prominent spots at $\sim 0.1$ and $\sim 0.165 \, \text{Å}^{-1}$ are found between the fundamental spots, Fig. 5(d). These spots nearly correspond to the $3/8$- and $5/8$-th fractional-order spots in (b). When the domains of three- and five-fold superstructures are separated as shown in Fig. 5(e), both of the five- and three-fold superspots are observed simultaneously, Fig. 5(f). The phase separation produces superspots of both superstructures. An interesting point is that the prominent spots in (d) are located in-between the five-fold and three-fold superspots in (f). Microscopic mixture of the different super-cells produces new spots located in-between.

At the intermediate Sr coverage between the 5$\times 1$ and 3$\times 1$ phases, the electron diffraction patterns consist of the five-fold and three-fold spots (left halves in Figs. 2(h)(i)). The results are reproduced in Fig. 5(f) and, therefore, large domains of the 5$\times 1$ and 3$\times 1$ phases are likely to coexist. On the contrary, the intermediate Ca coverage shows that the diffraction spots continuously shift from the five-fold to the three-fold superspots by coverage change, in other words, they located between the five-fold and three-fold spots (right halves in Figs. 2(h)(i)). Through a comparison between the simulated patterns in Fig. 5(d) and (f), one can find that the two spots in Fig. 5(d) is located just in the middle of the "5$x$" and "3$x$" spots. Thus, it is likely that the three-fold and five-fold structures are randomly distributed at the intermediate coverage between the 5$\times 1$-Ca to 3$\times 1$-Ca phases. Judging from the present results, there seems no long-range-order of a 8$\times 1$ superstructure by an alternate arrangement of the five- and three-fold unit cells. It is consistent to the previous STM research that has reported only local 8$\times 1$ domains at the intermediate Ca coverage [9].

We can now model that the three-fold and five-fold structures are randomly distributed during the 5$\times 1$-Ca to 3$\times 1$-Ca transition. Based on this scenario, we have also calculated variations of electron diffraction patterns during the transition as shown in Fig. 6. Through the decrease of area of the five-fold structures by inserting the 3$\times 1$ cells randomly, Figs. 6(a) to (i), the five-fold superspots continuously convert to the three-fold superspots, Figs. 6(b) to (j). This behavior completely reproduces the experimental results in Fig. 4(a).

Then, why does such a microscopic phase mixture occur? It must be related to two factors, surface (free) energy of each superstructure and boundary energy between different superstructures. According to a first-principles calculation [17], the 5$\times 1$ phase shows the lowest surface energy at a range of Ca chemical potential between those of the 3$\times 1$ and 2$\times 1$. Although there is no such calculations on the 7$\times 1$ and 9$\times 1$ phases, it is reasonable to assume that those phases have the lowest surface energy at intermediate Ca chemical potential (or Ca coverage), because the structural units of these $n \times 1$ structures are the same (HCC and Seiwatz chains). Since, however, the difference in surface energy is very subtle at the intermediate range of chemical potential as shown in Ref. [17], the neighboring phases can coexist at the intermediate coverage. As pointed out there, furthermore, entropic contribution to the surface free energy by intermixing the different $n \times 1$ stripes may be another important factor for the microscopic phase mixture. On the other hand, since a domain boundary between different phases generally costs some energy, such a microscopic phase mixture...
observed for Ca case means a negligible boundary energy. This is again reasonable because of the same structural units of these $n \times 1$ stripes. The difference we observed between Ca and Sr cases might be caused by differences in surface energy as a function of the chemical potential and the boundary energy due to differences in atomic size or ionic radii of the adsorbate metal atoms.

V. SUMMARY

We have observed a series of successive phase transitions in surface superstructures by changing the coverage of Ca or Sr on a Si(111) surface by use of RHEED. The most interesting finding is the transitions in the $n \times 1$ structures proceed by phase separation in Sr case, while by microscopic phase mixtures in Ca case. This difference is revealed by splits or continuous shifts of positions of fractional-order diffraction spots in RHEED.

Acknowledgments

This work has been supported by Grants-In-Aid from the Japanese Society for the Promotion of Science.
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