

Structure of the Ba-Induced Si(111)-(3 × 2) Reconstruction

Geunseop Lee,^{1,*} Suklyun Hong,² Hanchul Kim,¹ Dongsoo Shin,¹ Ja-Yong Koo,¹ Hyung-Ik Lee,¹ and Dae Won Moon¹

¹Materials Evaluation Center, Korea Research Institute of Standards and Science, Taejeon 305-600, Korea

²Department of Physics, Sejong University, Seoul 143-747, Korea

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The Ba/Si(111) surface, previously known as a 3×1 phase, is found to have a 3×2 periodicity and a semiconducting band gap. The substrate reconstructs into the honeycomb chain-channel (HCC) structure with Ba atoms in the channel, as in the alkali-metal-induced Si(111)-(3 × 1). However, the metal coverage is determined to be $1/6$ monolayers, half the alkali-metal coverage. We propose that the structure and the metal coverage determined for the Ba adsorbate is universal for other alkaline-earth-metal adsorbates. With the alkali-metal-induced 3×1 case, our results lead to a rule that one donated electron per 3×1 surface unit is necessary to stabilize the HCC reconstruction of Si.

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Over the past few years, one-dimensional (1D) structures on surfaces have been the focus of much interest due to their fundamental and technological importance. A number of metal/semiconductor systems have been reported to exhibit novel properties originating from the 1D structures: instability of the metallic phase and charge density wave transition for In/Si(111)-(4 × 1) [1], realization of non-Fermi liquid for Au/Si(111)-(5 × 1) [2], and Peierls-like gap opening for Au/Si(111)-(5 × 2) [3]. Another candidate for the 1D system is the Si(111)-(3 × 1) and Ge(111)-(3 × 1) surface whose reconstruction is induced by adsorption of alkali metals (AM = Li, Na, K, Rb) [4,5] and Ag [6]. The structure of the AM/Si(111)-(3 × 1) reconstruction was recently established [7–10] through the decade-long debates (see the references in Ref. [9]). The AM/Si(111)-(3 × 1) reconstruction adopts the so-called honeycomb chain-channel (HCC) structure, common to different metal adsorbates [9,10]. The AM atoms of $1/3$ monolayers (ML) [one metal atom per (3×1) unit cell] are located in the channels and form linear chains [11,12]. The surface was found to be semiconducting, in accordance with the one-electron picture. The AM/Ge(111)-(3 × 1) surfaces were found to have the similar reconstruction structure [13].

Adsorption of alkaline-earth metals (AEM = Mg, Ca, Ba) on the Si(111) surface was also known to induce the (3×1) phase, as observed in the low-energy electron diffraction (LEED) [14–16]. Recently, the interest on the AEM/Si(111)-(3 × 1) phase is growing because it offers a more interesting case as an 1D system than the AM/Si(111)-(3 × 1) surface. It has been suggested that the AEM/Si(111)-(3 × 1) phase has the same reconstruction and metal coverage as the AM/Si(111)-(3 × 1) surface [5,14]. If this is the case, the AEM/Si(111)-(3 × 1) surface should be metallic within the one-electron picture due to the addition of one more electron from AEM adsorbate [9], different from the case of semiconducting AM/Si(111)-(3 × 1) surfaces. On the other hand, if this metallic chain of AEM atoms embodies

the 1D structure, it is likely to be subject to structural modification [17].

Experimental data on the AEM/Si(111)-(3 × 1) phases are not consistent with the expectations. Photoemission studies on Mg/Si(111)-(3 × 1) [18] and Ca/Si(111)-(3 × 1) [19] showed that the surfaces are semiconducting: For its account, an electron correlation mechanism had to be introduced. On the other hand, the scanning tunneling microscopy (STM) studies provided a different perspective. A $\times 2$ periodicity was observed along the row in the empty state images from Mg/Si(111)-(3 × 1) [20] and Ca/Si(111)-(3 × 1) [21,22], while it was not observed in LEED. This period doubling would provide a natural explanation of the semiconducting property and can occur due to the instability of the 1D metallic chain via Peierls distortion and charge density wave formation [1–3]. Such an allegation would hold only provided that the metal coverage is truly $1/3$ ML in the structure similar to that of the AM/Si(111)-(3 × 1) surface. However, it should be noted that the metal coverage has never been measured in an *absolute* manner. In addition, no serious effort has been made to determine the structure for the AEM/Si(111)-(3 × 1) phase. A filled state STM image, where features specific to the Si substrate reconstruction appeared in case of AM/Si(111)-(3 × 1), has been recently reported only for Ca [19].

In this Letter, we determine the surface structure of the Ba/Si(111)-(3 × 1) phase by combining STM, absolute Ba coverage measurement using medium-energy ion scattering (MEIS), and *ab initio* pseudopotential calculations. It is found that the Ba/Si(111)-(3 × 1) phase is indeed a (3×2) surface consisting of the Si substrate reconstruction similar to that of AM/Si(111)-(3 × 1) and Ba atoms of $1/6$ ML coverage (half of the AM coverage). The surface is shown to be semiconducting, consistent with the (3×2) structure. The theoretical calculations based on this model reproduce quite well both the experimental STM images and the opening of a band gap.

Experiments were done in a ultrahigh vacuum chamber for STM and LEED measurement. The surface was prepared by evaporating Ba from a commercial dispenser (SAES Getters Inc.) onto the Si(111) substrate held at $\sim 850^\circ\text{C}$. While a sharp (3×1) pattern was observed in LEED with rather high background, no (3×2) feature was observed. The STM images were taken at room temperature. The Ba coverage was *ex situ* determined with a separate MEIS system.

Figure 1 shows a typical empty state image taken at a positive sample bias (V_s). Rows of protrusions run in the $[\bar{1}\bar{1}0]$ direction. The separation between the rows is $3a$, where $a = (\sqrt{3}/2)a_0$ [$a_0 = 3.84 \text{ \AA}$, a unit lattice spacing on a bulk-terminated Si(111) surface]. Within the row, the spacing of the successive protrusions is $2a_0$. The protrusions in the neighboring rows form either (3×2) or $c(6 \times 2)$ local arrangement, depending on their relative positions. The STM image clearly shows that this Ba/Si(111) surface indeed has a (3×2) structure while LEED intensities of the half-order spots or streaks were not detected [16]. Nearly identical STM features were observed for the Si(111)- (3×1) phases induced by other AEM adsorbates, Mg [20] and Ca [21,22]. The (3×2) protrusions in the empty state image are interpreted to be AEM atoms occupying a specific site, in the same way as for the AM/Si(111)- (3×1) case.

The Si substrate reconstruction of the Ba/Si(111)- (3×2) surface can be deduced from the filled state STM image shown in Fig. 2(a). There are bright double rows running in the $[\bar{1}\bar{1}0]$ direction. The protrusions in the double rows form zigzag chains with the apparent $\times 1$ periodicity. The zigzag chain feature in the filled state image is nearly identical to that reported for the AM-induced Si(111)- (3×1) surfaces, except for abundance of defects.

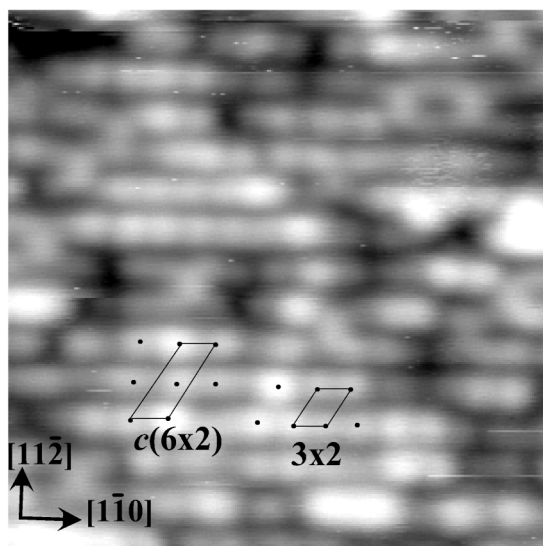


FIG. 1. An empty state STM image of Ba/Si(111)- (3×1) acquired at $V_s = +2.0 \text{ V}$. The protrusions form local arrangement of either (3×2) or $c(6 \times 2)$, as outlined in the figure.

Thus those protrusions are assigned to Si atoms. It suggests a close resemblance of the Ba/Si(111)- (3×2) substrate structure to that of AM/Si(111)- (3×1) , basically having the same (3×1) Si reconstruction. However, a careful scrutiny of the image reveals period doubling as indicated in Fig. 2(b). This implies that the filled state image, similar to the empty state image, shows the $\times 2$ periodicity. This feature is very similar to that of the recent filled state image of Ca/Si(111)- (3×1) [19].

The $\times 2$ period along the row in the empty state image may suggest a formation of a Peierls distortion or a charge-density wave with a Ba coverage of $1/3 \text{ ML}$ [19,21], or alternatively, a coverage of $1/6 \text{ ML}$. The measurement of the absolute quantity of metal atoms on the surface is necessary in differentiating two scenarios. The STM is, however, not a suitable tool to determine the coverage. MEIS, which is a high-resolution version of Rutherford backscattering spectroscopy [23], was used to determine quantitatively the Ba atom density on the surface [24]. The amount of Ba atoms on the Ba/Si(111)- (3×2) surface was measured to be $1.33 \times 10^{14} \text{ atoms/cm}^2$. This corresponds to 0.17 ML ($1 \text{ ML} = 7.83 \times 10^{14} \text{ atoms/cm}^2$) and is close to the value of $1/6 \text{ ML}$. This Ba coverage is significantly smaller than the previously measured value of 0.35 ML as an upper limit using Auger electron spectroscopy (AES) [16]. We believe that the coverage measurement using AES can be subject to an error because it relies on some assumptions. The $1/6 \text{ ML}$ Ba coverage is unexpected in that $1/3 \text{ ML}$ of AEM has been presumed by analogy with the case of AM/Si(111)- (3×1) .

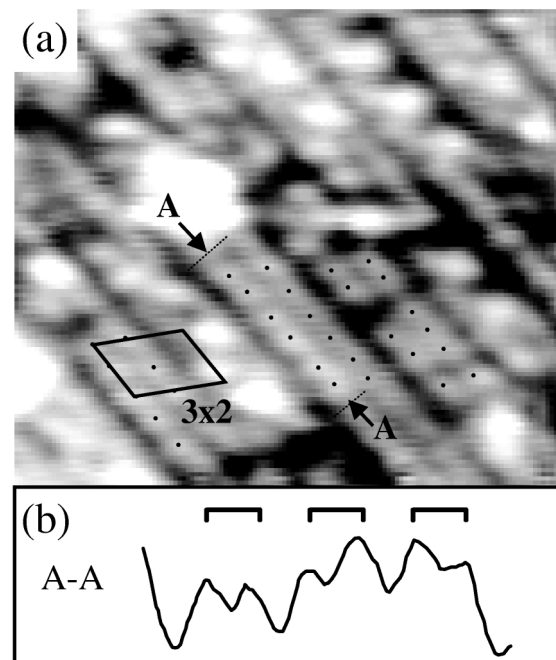


FIG. 2. (a) A filled-state STM image of Ba/Si(111)- (3×2) acquired at $V_s = -2.0 \text{ V}$. Note that the protrusions in a double row form a zigzag chain (marked by dots). (b) Surface height profile along A-A in (a) revealing the $\times 2$ pairing.

The atomic structure of the Ba/Si(111)-(3 × 2) surface can be constructed based on the two basic findings: (i) the Si substrate reconstruction similar to the AM/Si(111)-(3 × 1) surface and (ii) the Ba coverage of 1/6 ML. We consider only the HCC structure, the most favored reconstruction for the AM/Si(111)-(3 × 1) surface, while a different model was previously proposed for Mg and Ca [25]. The HCC structure is also consistent with the topmost layer Si density of 4/3 ML determined for Mg and Ca as well as the AM adsorbates [26].

To validate the HCC model with 1/6 ML Ba for the Ba/Si(111)-(3 × 2) surface, we have performed *ab initio* calculations within the local density approximation (LDA) using the Vienna *ab initio* simulation package (VASP) [27]. The atoms are represented by ultrasoft pseudopotentials as provided with VASP [28]. The Ba/Si(111)-(3 × 2) surface is modeled by a slab which is composed of a Ba atom, eight Si atoms forming honeycomb chains, four Si layers, and an H layer passivating the bottom surface. We used a kinetic energy cutoff of 150 eV. The constant-current STM images are simulated within the Tersoff-Hamann scheme [29].

The 1/6 ML Ba coverage was accommodated by putting one Ba atom in every second (3 × 1) unit cell of the HCC structure. Three different sites, T₄, H₃, and B₂ [see Fig. 3(a)], were tested. The surface energies for T₄ and H₃ sites are comparable (the former being lower by 0.01 eV/Ba), while that of the B₂ site is much higher (by 0.15 eV/Ba). The equilibrium geometry and the simulated STM images are shown in Fig. 3 for the T₄ site. The presence of Ba atoms in every other (3 × 1) subunit induces a structural modification in the honeycomb chain. Most prominently, the neighboring honeycombs are deformed inequivalently: One honeycomb is more elongated in the [11 $\bar{2}$] direction, perpendicular to the chain, than the adjacent ones. The other noticeable deformation occurs at the left edge of the honeycomb chain [denoted as *l* in Fig. 3(a)]: Along the chain, the corrugations are 0.13 Å in height and 0.4 Å in the lateral displacement perpendicular to the chain, respectively. In the right edge [denoted as *r* in Fig. 3(a)], the deformation is hardly recognizable. Consequently, the substrate reconstruction, as well as the Ba adsorption, adopts ×2 periodicity along the chain direction. Two inner Si atoms of each honeycomb form a double bond, as in the case of AM/Si(111)-(3 × 1). The double-bond length is 2.25 Å.

The simulation well reproduces the experimental STM images both for the empty states and for the filled states. In the empty state image [Fig. 3(a)], the bright protrusions with ×2 periodicity along the row reflect the Ba atoms. In the filled state image [Fig. 3(b)], the zigzag shape connecting two neighboring honeycombs across a channel is the manifestation of the saturated dangling-bond states of the Si atoms surrounding Ba. A closer look at the filled state STM image unveils a pairing of Si atoms in the *r* row, in good agreement with the observed pairing

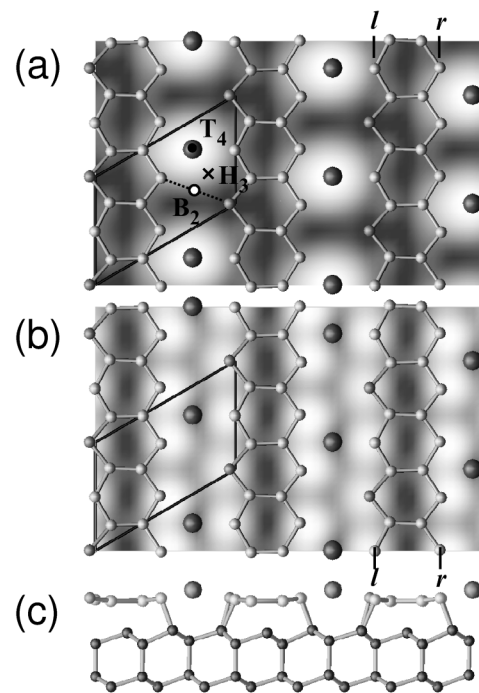


FIG. 3. The simulated STM images of (a) the empty state ($V_s = 2$ V) and (b) the filled state ($V_s = -2$ V). The top view of the surface is overlapped with the images and the side view is shown in (c), where the large (small) balls represent Ba (Si) atoms, respectively. Denoted in (a) are the three Ba adsorption sites in the channel.

in the experimental image [along A-A in Fig. 2(a)]. The pairing is caused by the electrostatic attraction between a positive Ba ion and the electrons in two neighboring saturated dangling bonds on the *r*-row Si atoms. In other words, the pairing observed in the filled-state images is Ba-assisted. Similarly, a Ba ion attracts the dangling bond electrons of the nearest Si atom in the *l* row. This compensates the corrugation in lateral displacement (where the Si atom moves away from the Ba chain) and results in almost aligned bright spots in the *l* row.

The tunneling spectroscopy on the Ba/Si(111)-(3 × 2) surface showed that the surface is semiconducting with a band gap of 1.0 ± 0.1 eV. The semiconducting property can be easily understood by the fact that the true unit cell of this surface is (3 × 2). From electron counting, the (3 × 2) unit cell contains an even number of electrons and fulfills a prerequisite for a nonmetallic ground state within a band theory, regardless of the Ba coverage. The magnitude of the band gap, however, depends on the Ba coverage within the HCC-based Si substrate reconstruction structure. The band gap calculated for our HCC model with 1/6 ML Ba atoms is 0.7 eV and reasonably well reproduces the experimental value considering that the LDA tends to underestimate the band gap. In contrast, the HCC structures with 1/3 ML Ba have a much smaller gap (≤ 0.35 eV), although a period change from (3 × 1) to (3 × 2) can be introduced in several ways [30].

It is concluded that the apparent AEM/Si(111)-(3 × 1) phases as viewed in LEED indeed possess a (3 × 2) structure with metal coverage of 1/6 ML, instead of 1/3 ML. Both the (3 × 2) periodicity and the semiconducting property are naturally explained by the 1/6 ML metal coverage. Any mechanism related to the 1D structure, such as the charge density wave or the electron-electron correlation proposed for the Ca case [19], are not necessary. The main obstacle to our conclusion would be the fact that the (3 × 2) LEED pattern is hardly observable for these phases. The reason for the apparent conflation between LEED and STM is not clear. We conjecture that the absence of the half-order spots or streaks originates from the lack of long-range order. The STM images of the Ba/Si(111)-(3 × 2) surface (Figs. 1 and 2) show that the long-range order in the chain direction is poor due to the presence of numerous defects. The lack of long-range order is also consistent with the high background intensity in LEED. This situation is quite analogous to the case of the Au/Si(111)-(5 × 2) system where the confusion between ×1 and ×2 periodicities have prevailed based on LEED observation [2,3]. However, a very recent study [26] using spot-profile-analysis LEED successfully observed the half-order streaks for Ca/Si(111)-(3 × 2), supporting our speculation.

It is interesting to note that the structure of the Si substrate reconstruction is common for both AM and AEM adsorbates despite the difference in metal coverage. However, one should pay attention to the fact that *the number of electrons donated by the metals are same for both cases*—one electron per (3 × 1) unit cell. It may implicate that the Si(111) surface tends to reconstruct into the (3 × 1) surface with the HCC structure provided that a right amount of electrons are supplied and saturate the Si dangling bonds. The deformation of the honeycomb chain and the period doubling in case of the AEM adsorbates can be regarded as a minor perturbation from the basic (3 × 1) HCC structure.

In summary, the structure of the semiconducting Ba/Si(111)-(3 × 2) surface has been determined from the combined study of STM, MEIS, and *ab initio* calculations. The substrate Si reconstruction is similar to that of AM/Si(111)-(3 × 1), the HCC structure, but the Ba coverage of 1/6 ML is unexpectedly smaller. We propose that this structure is commonly adopted for other AEMs such as Mg and Ca. Furthermore, from AM/Si(111)-(3 × 1) and AEM/Si(111)-(3 × 2) cases, we suggest a general rule: One donated electron per (3 × 1) unit is necessary to form the HCC reconstruction of the Si substrate.

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*Corresponding author.

Email address: glee@kriss.re.kr

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