Ca-induced intermediate reconstructions on the Si(111) surface

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The geometric and electronic properties of the Ca-induced intermediate reconstructions on the Si(111) surface, particularly Ca/Si(111)-(5 × n) with n = 1, 2, and 4, are theoretically investigated using the pseudopotential method and the local-density approximation (LDA) of the density-functional theory. The geometrical models for the three reconstructions are based on deposition of different Ca lines on the top of a combination of a honeycomb chain channel and a Seiwatz chain formed by Si atoms. These structural models are found to produce semiconducting surface band structures with clear LDA energy gaps. We have identified one, three, and four surface states within the bulk band gap for the (5 × 1), (5 × 2), and (5 × 4) reconstructions, respectively. The relative stabilities of these reconstructions are discussed as a function of Ca coverage. Significant charge transfer from the Ca adatoms to neighboring Si atoms has been concluded by analyzing electronic charge density and scanning tunneling microscopy simulations.

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I. INTRODUCTION

Studies of elemental adsorption on semiconductor surfaces have been carried out intensively both experimentally and theoretically in the past few decades. Recently, there has been much effort devoted to fabricating nanometer-scale electronic devices using self-assembled quasi-one-dimensional (1D) overlayer structures. Many of such structures have been fabricated by depositing metallic elements on semiconductor surfaces. Of potential technological importance and scientific interest is the physics of metal adsorbed Si(111) surfaces. On this surface quasi-1D structures have been fabricated by depositing group-I, group-II, and group-III elements with some examples of adsorbates being: noble metals (such as Au), alkali metals (such as Li, Na, etc.), alkaline-earth metals (such as Ca, Mg, etc.), and In. While only a few well-established reconstructions are known to take place for the deposition of monovalent and trivalent metal adsorbates on Si(111), it has been reported that a large number of reconstructions exist for divalent metal adsorbates. Moreover, while structural models and electronic properties of quasi-1D group-I/Si(111) and group-II/Si(111) systems are well established, not enough work has been carried out on quasi-1D group-II/Si(111) to completely understand their geometry and electronic structure.

In particular, several groups have demonstrated that a series of reconstructions can be achieved by depositing different amounts of submonolayer coverage of alkaline-earth metal Ca on Si(111). Generally, the Ca/Si(111) surfaces are prepared by following two different deposition procedures (see, e.g. Ref. 7). Either a certain amount of Ca is deposited onto the clean Si(111)-(7 × 7) surface with subsequent annealing at approximately 825 K, or a reduced amount of 0.5 monolayer (ML) of Ca is deposited onto the clean Si(111)-(2 × 1) surface and annealed between 900 and 1050 K. The reported lowest and highest coverages of Ca are 1/6 and 1/2 monolayers (ML), and result in the (3 × 2) and (2 × 1) reconstructions of the surface, respectively. Between these two coverages, a large number of other reconstructions have been reported. With increasing Ca coverage at elevated substrate temperatures, a series of odd-order (n × 1) reconstructions, with n = 3, 5, and 7, are established by reflection high energy electron diffraction (RHEED) and scanning tunneling microscopy (STM). The (3 × 1) and (5 × 1) reconstructions correspond to Ca coverages 1/3 and 2/5 ML, respectively. More recently, (5 × 2) (Ref. 9) and (5 × 4) (Ref. 10) low-energy electron-diffraction (LEED) patterns have also been observed. These both correspond to the Ca coverage of 1/3 ML. With increase in Ca coverage, all these reconstructions culminate with the (2 × 1) reconstruction. The lowest coverage (3 × 2) phase is explained in terms of a honeycomb channel (HCC) chain structure and the highest coverage (2 × 1) reconstruction is believed to exhibit a Seiwatz (SZ) chain structure. The intermediate phases can be considered to be formed as a combination of the HCC and SZ motifs. Miwa performed ab initio calculations on the (3 × 2), (3 × 1), and (2 × 1) reconstructions, and concluded that the (3 × 1) reconstruction is not expected to occur even under Ca-rich conditions. His calculations also presented a qualitative picture for the core-level photoemission results obtained by Sakamoto et al.

Sakamoto and co-workers attempted to investigate the atomic geometry of the Ca/Si(111)-(5 × 1) surface by using LEED and high-resolution core-level photoelectron spectroscopy. They concluded that the (5 × 1) reconstruction, corresponding to 0.4 ML coverage of Ca, is not stable. In fact, these researchers proposed a stable (5 × 2) phase with a Ca coverage of 0.3 ML with Ca atoms adsorbed on tetrahedral fourfold (T4) and hollow threefold (H3) sites along the surface trench. For this coverage there is an even number of valence electrons per (5 × 2) unit cell and the system exhibits semiconducting behavior. Similarly, the same group has proposed a structural model for the Ca/Si(111)-(5 × 4) system for the Ca coverage of 0.3 ML. It has been reported that all of the Ca/Si(111)-(5 × n) reconstructions, with n = 1, 2, and 4, are semiconducting and that almost all of the valence charges on Ca atoms were transferred to neighboring Si atoms. Experimental results obtained from angle-resolved photoelectron spectroscopy (ARPES) from valence electrons have revealed at least three surface states within the bulk gap region for Ca/Si(111)-(5 × 2) and five surface states for...
Ca/Si(111)-(5 × 4). Despite many experimental studies, however, no theoretical investigations have been reported so far on the equilibrium atomic geometry and electronic characteristics of the Ca/Si(111)-(5 × 1), -(5 × 2), and -(5 × 4) surfaces.

In this paper, we present results of first-principles calculations, based on the pseudopotential method and the density-functional scheme, of the atomic geometry, electronic properties, and identity of atomic orbitals on Ca adsorbed (5 × 1), (5 × 2), and (5 × 4) reconstructions on Si(111). We further discuss the relative stabilities of these reconstructions.

II. Theory Method

Our calculations were performed in the framework of the density-functional theory, within the local-density approximation (LDA) using the Ceperley-Alder correlation, as parametrized by Perdew and Zunger. Electron-ion interactions were treated by using norm-conserving, as parametrized by Perdew and Zunger. Electron-ion interactions were treated by using norm-conserving, ab initio, fully separable pseudopotentials in the framework of Bachelet, Hamann, and Schlüter scheme, with the following core radii: \( r_p = r_s = 3.09 \) a.u. for Ca, \( r_p = r_s = 2.0 \) a.u. for Si, and \( r_s = 1.25 \) a.u. for H. The single-particle Kohn-Sham wave functions were expanded in a plane-wave basis set with a kinetic-energy cutoff of 15 Ryd for (5 × 1) and (5 × 2) while 8 Ryd is used for (5 × 4) due to its heavy computational framework. Surface calculations were performed by adopting the repeated slab method with a supercell containing four silicon layers, the Si chain-atoms layer, the Ca adatom layer, and a vacuum region equivalent to 2.5 times the bulk lattice constant. The Si dangling bonds at the bottom layer were saturated with hydrogen atoms. The equilibrium atomic positions were determined by relaxing all atoms except the bottom layer of Si, which was kept fixed. The Hellmann-Feynman forces on ions were calculated and minimized to obtain the relaxed atomic geometry. Atoms were relaxed until forces converged to within 10 meV/Å. The electronic charge density was calculated by using a \( 1 \times 4 \times 1, 1 \times 2 \times 1, \) and \( 1 \times 1 \times 1 \) \( \mathbf{k} \)-points Monkhorst-Pack set for (5 × 1), (5 × 2), and (5 × 4), respectively.

III. Results and Discussion

Our structural models for the (5 × \( n \)) reconstructions on the Ca/Si(111) surface are considered to be based on Ca line formation above the top atomic Si(111) layer, which itself is reorganized in the form of a combination of the SZ and the HCC chains. We will discuss the results of formation energy, atomic geometry, and electronic structure for each system, and present a comparative study.

A. Ca/Si(111)-(5 × 1)

1. Adsorption site

For the Ca/Si(111)-(5 × 1) surface with a Ca coverage of 0.4 ML, we considered two Ca lines—labeled as A and B lines. The Ca atoms along each of the two lines were initially considered to adopt two different adsorption sites: \( T_3 \) (where the Ca atoms lie just above the second unreconstructed layer of Si atoms) and \( H_3 \) (where the Ca atoms reside just above the fourth unreconstructed layer of Si atoms). The energy minimum structures for both models are shown in Fig. 1. It is found that the \( T_3 \) site is energetically more favorable than the \( H_3 \) site with an energy gain of 19 meV/atom. The theoretical determination of the energetically favorable \( T_3 \) site is in agreement with the analysis of the core-level photoemission data by Sakamoto et al.

2. Relaxed atomic geometry

From our calculations we first note that for the clean Si(111)-(5 × 1), the length of the Si-Si bonds in the Si chain layer, as well as in the bilayer below the chain layer, is 2.32 Å, which is almost equal to the bulk bond length. For the Ca/Si(111)-(5 × 1) structure, the average bond length in the Si chain layer is 2.25 Å and that in the bilayer below the chain layer is 2.32 Å. This suggests that the Ca adsorption leads to shortening of the bond length in the Si chain layer. The calculated relaxed geometry of the Ca/Si(111)-(5 × 1) structure (Fig. 1) shows that Ca(A) and Ca(B) lines are, respectively, at 1.0 and 1.27 Å above the top substrate Si layer. The HCC chain is tilted with a buckling of 0.35 Å and the SZ chain is buckled by 0.3 Å. These tilt values are of almost the same amount as those obtained for the clean surface. The atomic layer forming the Si chain layer is pushed down by 0.15 Å due to the Ca adsorption. However, no appreciable movement was noticed for the second bilayer. The characteristic structural parameters are presented in Table I(a).
TABLE I. Key structural parameters of the relaxed geometry for the Ca/Si(111)-(5×1), (5×2), and (5×4) phases with 0.4, 0.3, and 0.3 ML coverage of Ca atoms. Numbers 1–4 refer to silicon adatoms nearest to Ca adatoms and numbers 1′–4′ refer to atoms in the first Si(111) layer, as shown in Figs. 1, 6, and 8.

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<th>CaA−2</th>
<th>CaB−3</th>
<th>CaB−4</th>
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<th>2−2′</th>
<th>3−3′</th>
<th>4−4′</th>
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3. Electronic calculations

The electronic band structures for both clean and Ca covered Si(111)-(5×1) surfaces have been calculated along a line perpendicular to the HCC chain, indicated as Γ−J in Figs. 2(a) and 2(b). For the clean surface, we have identified three surface states inside the Si bulk band-gap region: an occupied state near the zone edge, an unoccupied state in the middle of the gap, and another unoccupied state close to the zone center just below the bulk projected region. The minimum surface band gap is smaller than the minimum bulk band gap. Upon Ca adsorption, the occupied surface state and the upper-lying unoccupied states of the clean surface are pushed inside the bulk band regions. The lower-lying unoccupied state of the clean surface is pushed up and becomes a true surface state from Γ up to $\frac{\Gamma}{2}J$. The resulting band gap is approximately 0.33 eV, much smaller than the bulk band gap. In order to clarify the atomic origins of the surface band structure, we examine in Figs. 2(c) and 2(d) the charge density of the highest occupied (S1) and lowest unoccupied (S2) surface states. As seen in Fig. 2(c), the highest occupied surface state is primarily localized around the buckled Si atoms forming the edges of the HCC chain and the lowest unoccupied surface state is largely localized on the upper-lying Si atoms forming the HCC chain.

Figure 3(a) shows the density of states (DOS) for the Ca/Si(111)-(5×1) surface. Also shown, for comparison, is the bulk DOS. The shoulder in the bulk DOS at around $E_v + 0.4$ eV has turned into a well developed peak (C1) after Ca adsorption. Much more significant changes in the DOS curve have taken place in the valence-band region between $E_v$ and $E_f$.
interpretation of the peaks creases dramatically with the increase in Ca coverage. Our \( \text{Ca} \) calculated Fermi energy, as shown in Fig. 5.

Following the Tersoff-Hamann scheme,\textsuperscript{25} we produce simulated STM images at constant height just above the \( \text{Ca(B)} \) atom for the energy bias \( \pm 2.0 \) eV with respect to the calculated Fermi energy, as shown in Fig. 5(a). The filled-state image (left panel of Fig. 5) shows three bright lines: two of these are at the edges of the HCC chain and the third one is at one end of the SZ chain. These lines are closest to the Ca atomic lines, suggesting that these protrusions are significantly contributed by the electronic charge transfer from the Ca 4s orbitals. The positive bias image (right panel of Fig. 5) is contributed by the \( p_z \) orbitals of the Si chain atoms underneath the Ca lines. The unoccupied STM image is brighter along the HCC chain with equal brightness at each of the atoms, forming hexagons. The SZ chain is slightly less bright with almost equal intensity at the two component atoms of the chain. Our simulated STM images are quite similar to those obtained theoretically by Baski et al.

**B. Ca/Si(111)-(5\times2)**

### 1. Relaxed atomic geometry

In this structural model, the Ca atoms are considered to be adsorbed at both \( T_4 \) and \( H_3 \) symmetry sites. As schematically shown in Fig. 6, two thirds of Ca atoms are adsorbed at \( T_4 \) sites (along the lines indicated with \( A \) and \( B \)) and the remaining one third of all Ca atoms are adsorbed at \( H_3 \) sites (along the line indicated with \( C \)). The \( A \) and \( B \) lines are the same as on the \( (5\times1) \) surface except that the concentration of Ca atoms is halved (i.e., every alternate Ca atom along the \( A \) and \( B \) lines of the \( (5\times1) \) reconstruction is removed when considering the \( (5\times2) \) reconstruction). The Ca atoms along the line labeled \( C \) lie between the SZ chain on the left side and the HCC chain on the right side, and to the right of the Ca(B) atom. The Ca atoms along the \( B \) and \( C \) lines are seen to be arranged in a zigzag chain configuration.
The key structural parameters of the equilibrium geometry from our theoretical calculations are shown in Table I. The Ca atoms along the A and C lines at T sites are essentially at the same height, lying approximately 0.17 Å above Ca atoms along the B lines at T sites. The Ca atoms at the A, B, and C sites are at distances 3.02, 3.25, and 2.38 Å, respectively, from their nearest Si neighbors. The distance between the Ca(C) and its neighboring Si is much shorter than the sum of the atomic radii of Ca and Si. This agrees very well with the analysis of the core-level photo-

FIG. 4. (Color online) Total charge-density plots along various lines joining Ca atoms with their neighboring Si chain atoms on the (a) (5×1), (b) (5×2), and (c) (5×4) Ca/Si(111) surfaces.
emission data by Sakamoto et al.\textsuperscript{9} The bond length between the chain Si and the first-layer Si(111) atoms is slightly longer than the bulk bond length, and ranges between 2.37 and 2.39 Å. This indicates that the bonding between the Si chain layer and the first layer Si(111) is slightly weaker than the bulk bonding. The SZ chain is buckled with a vertical separation between “up” and “down” atoms of approximately 0.31 Å. No appreciable buckling of the HCC atoms was noted. Upon the adsorption of the Ca lines, the Si chain layer is pushed down (toward the bulk) by approximately 0.20 Å.

It is instructive to compare the relaxed geometry of the (5 × 2) surface with the (5 × 1) surface. The atomic positions of Ca atoms along the \( A \) line remain almost the same for the two reconstructions. The Ca\((C)\) atom for (5 × 2), of course, has no counterpart for (5 × 1). The lengths of the Si-Si back bonds remain essentially the same for both (5 × 2) and (5 × 1). However, the following differences between the relaxed geometries for the (5 × 2) and (5 × 1) reconstructions have been found. The Ca\((B)\) atom on the (5 × 2) surface resides at a larger distance from the neighboring Si atom [viz. 3.25 Å for (5 × 2) compared to 3.07 Å for (5 × 1)]. While the HCC chain shows no buckling for the (5 × 1) reconstruction, it is heavily buckled by 0.35 Å for the (5 × 2) reconstruction. We believe that the large buckling of the HCC chain on (5 × 2) results from the presence of the \( C \) lines of Ca atoms.

2. Electronic calculations

The electronic band structures of the Ca/Si(111)-(5 × 2) and clean Si(111)-(5 × 2) surfaces were calculated along the shortest direction toward the surface Brillouin-zone boundary (viz. the \( \Gamma - J \) direction). This direction corresponds to a line perpendicular to the SZ and HCC chains. As seen in Figs. 7(a) and 7(b), both systems are semiconducting with the LDA band gaps, at the \( \Gamma \) point, of approximately 0.56 and 0.43 eV, respectively. For the clean Si(111)-(5 × 2) surface, we have identified one localized occupied state just below the bulk valence-band maximum toward the zone edge. On the other hand we have identified up to three localized unoccupied states just below the bulk conduction-band minimum for all \( \mathbf{k} \) points from the zone center toward the zone edge. The energy locations and dispersions of these surface states can in fact be obtained from a folding of the surface states on Si(111)-(5 × 1). As the clean (5 × 1) and (5 × 2) surfaces exhibit semiconducting behavior, it is clear that the formation of the SZ and HCC chain structures has resulted in an effective “electronic passivation” of the Si(111) surface. However, due to some empty dangling bonds on the SZ and HCC chains, the clean surface systems remain partially “chemically unpassivated.”

For the Ca covered surface, we have identified up to two localized occupied states just below the bulk valence-band maximum toward the zone edge and one localized unoccupied state just below the conduction-band minimum near the zone center. In Figs. 7(c)(i)–(ii), 7(c)(iii), and 7(c)(iv) we present the partial charge-density plots of the highest occupied and the lowest unoccupied states on the Ca covered...
surface together with the lowest unoccupied state for the clean Si(111)-(5×2) surface. The lowest unoccupied state on the clean surface is localized on the down Si atoms of the tilted SZ chain, made largely of the p_z orbital with a small contribution from the s orbital. Upon Ca adsorption, this state is filled and resonates with bulk states. The highest occupied state of the Ca/Si(111)-(5×2) system is dominantly localized at the edges of the HCC chain close to Ca(A) with an sp_z orbital character. The lowest unoccupied state of the Ca/Si(111)-(5×2) system is localized at the HCC chain far from Ca(A) and Ca(C) with a large p_z orbital character. This results in a better “passivation” of the Si(111) surface with Ca coverage, both electronic and chemical.

Figure 3(b) shows the DOS for the Ca/Si(111)-(5×2) surface. For comparison, we have also presented the Si bulk DOS. Of practical importance are the regions from \(-E_c + 0.5\) eV to \(-E_c - 2\) eV. In the valence-band region we have identified three surface peaks. Two of these peaks, V1 and V2 at approximately \(-1\) eV and \(-2\) eV, respectively, are pretty close to the two corresponding peaks on the (5×1) surface. The third peak, V0 at approximately \(-0.5\) eV, is a shoulderlike feature in the DOS for the 5×2 surface. The origins of the peaks V1 and V2 are the same as on the (5×1) surface. We tentatively assign the peak V0 to originate from the relaxation of Si atoms closest to the third line of Ca atoms on the (5×2) surface [viz. Ca(C) atoms]. In the conduction-band region, the surface peak C1 on (5×2) lies at a slightly higher energy (\(E_c + 0.5\) eV) than for the (5×1) surface, in agreement with the band-structure results in Figs. 6(b) and 7(b). Also, C1 is more intense on (5×2) than on (5×1): the peak ratio V2/C1 is larger for (5×1) than for (5×2).

For a further understanding of the electronic properties, we performed STM image calculations at a fixed height [just above the Ca(A) adatom], and for an energy interval of 2.0 eV above and below the calculated Fermi energy. The results are shown in Fig. 5(b). The main contributions to the occupied states (left panel of Fig. 5) originate from the topmost Si atoms forming the SZ chain. It is also clear that the positive bias STM image (right panel of Fig. 5) is formed by unoccupied surface states belonging to the double-bonded Si atoms of the HCC chain. The changes in the STM images,
going from \((5 \times 1)\) to \((5 \times 2)\), can be directly related to (i) the insertion of the Ca(C) line, and (ii) reduction in the concentration of Ca atoms along the A and B lines for the \((5 \times 2)\) structure.

We have employed a very simple scheme to estimate charge transfer from the Ca atoms toward their neighboring Si atoms. For this, we have calculated the total charge density in a sphere around a Ca atom of radius equivalent to the distance between the Ca atom and the nearest Si atom. Using the same procedure we determined the charge around a single Ca atom placed in the unit cell that was used for the surface calculations. Using the numerical results from these two calculations, we find that approximately 0.98\(e\) charge has been transferred from each Ca atom to its neighboring Si atoms. This is in good agreement with the total charge-density plots shown in Fig. 4(b) along Si\_SZ-Ca(C)-Si\_HCC, Si\_SZ-Ca(B)-Si\_HCC, Si\_HCC-Ca(A)-Si\_SZ, and Ca(C)-Ca(B).

Evidently, Ca(C) has transferred more charge to the HCC chain than to the SZ chain, and Ca(B) has transferred almost similar amounts of charge to the SZ chain and the HCC, with a slightly more charge to the HCC. However, in contrast to \((5 \times 1)\), Ca(A) on \((5 \times 2)\) has transferred approximately equal amount of charge to both HCC and SZ chains. In addition, we find that there is no clear bonding between Ca(C) and Ca(B), as the maximum of the charge density along the line joining these atoms is an order of magnitude smaller than the maximum along the Ca-Si lines. Comparing the \((5 \times 2)\) with the \((5 \times 1)\), it can therefore be noted that there is effectively more charge transfer from Ca atoms to the HCC for the former structure.

C. Ca/Si(111)-(5\times4)

Although we have considered the \((5 \times 2)\) reconstruction for 1/3 ML coverage of Ca, as suggested in the work by Sakamoto et al., there is some uncertainty about the coverage for this reconstruction. For example, Baski et al.\(^5\) and Sekiguchi et al.\(^6\) have estimated the coverage to be 0.4 ML. The 1/3 ML coverage of Ca, however, has been reported to produce a clear \((5 \times 4)\) reconstruction. From an analysis of core-level photoemission spectra, Sakamoto et al.\(^10\) proposed two structural models for the Eu/Si(111)-(5\times4) surface with a coverage of 1/3 ML. In one model, called the H\(_3\) model, each \((5 \times 4)\) surface unit mesh contains four Eu atoms adsorbed on the T\(_4\) site and two Eu atoms on the H\(_3\) site. In the second model, called the B\(_2\) model, each surface unit cell contains four Eu atoms on the T\(_4\) site and two Eu atoms on the twofold bridge (B\(_2\)) site. Although no strong evidence could be found in favor of either of the structural models, it was the B\(_2\) model that was eventually proposed. This model was subsequently proposed for the Ca/Si(111)-(5\times4) surface by Sakamoto et al.\(^11\) Based on the consideration that intermediate-coverage structures can be formed as a combination of the \((3 \times 2)\) (HCC) and \((2 \times 1)\) (SZ) structures involving T\(_2\) and H\(_3\) sites, it is more logical to consider the H\(_3\) model for the Ca/Si(111)-(5\times4) surface. In this work we have, thus, used the H\(_3\) model for the 1/3 ML coverage forming the Ca/Si(111)-(5\times4) surface.

The H\(_3\) model for the Ca/Si(111)-(5\times4) surface can be described by remembering that the \((5 \times 2)\) structure consists of two lines of Ca atoms on the T\(_4\) sites (the lines A and B in Fig. 6) and one line of Ca atoms on the H\(_3\) sites (line C in Fig. 6). For the \((5 \times 4)\) structures, the lines A, B, and C are retained, and a fourth line of Ca atoms at the H\(_3\) sites (indicated as line D in Fig. 8) is added. Thus the H\(_3\) model contains four atoms in T\(_4\) sites (lines A and B) and two atoms at the H\(_3\) sites (lines C and D).

1. Relaxed atomic geometry

Figure 8 shows schematic side and top views of the optimized structure. Numerical values of detailed atomic geometry are given in Table I(c). The Ca atoms on the B line reside at the same height (0.945 Å above the Si chain layer). There is a huge vertical buckling of 0.89 Å between the two Ca atoms along the A line. The Ca(C) and Ca(D) atoms are at the same height, lying well above the Ca(B) atoms but intermediate to Ca(A1) and Ca(A2) atoms. The Si chain is pushed down toward the Si(111) surface by 0.15 Å. The bond length of Si-Si chain atoms is 2.28 Å. This bond length is shorter than the bulklike bond length by approximately 3.0%, suggesting a strong and more stable surface. In contrast, the bond length of Si-Si atoms just underneath the Si chain is 2.34 Å. Once again, this bond length is very comparable with the bulk bond (2.35 Å). The bottom layers are quite similar to the starting geometry. The buckling in the SZ chain is approximately 0.23 Å. Moreover, the HCC chain is tilted by 0.12 Å.

The formation of the \((5 \times 4)\) structure has allowed for additional relaxation compared to the \((5 \times 2)\) surface. The

![Figure 8](https://example.com/fig8.png)
Ca-INDUCED INTERMEDIATE RECONSTRUCTIONS ON...  

![Band structure plots](image)

**FIG. 9.** (Color online) Upper Panel: Electronic band structure for (a) the clean Si(111)-(5×4) surface and (b) the Ca-covered Si(111)-(5×4) surface along a direction perpendicular to the Ca lines. The empty circles represent the experimental data obtained from Ref. 11 and the dashed lines are the resonant surface states. The surface Brillouin zone is indicated. Lower Panel: Partial charge-density plots in a horizontal plane passing through the Si chain atoms at the Γ point for the four surface states labeled S1–S4 in the band-structure plot.

Ca(A1) and Ca(A2) atoms are significantly further from their neighboring Si atoms for the (5×4) than for (5×2). In contrast, the Ca(B1) and Ca(B2) atoms on the (5×4) are at slightly shorter distance from their neighboring Si atoms than on the (5×2) surface. The distance between the Ca(C) atom and its neighboring Si atom has increased from its value for the (5×2) surface.

2. Electronic calculations

In order to investigate the surface band structure of the Ca/Si(111)-(5×4) phase, we present in Figs. 9(a) and 9(b) the results for both clean and Ca-covered (5×4) surfaces around the Fermi level. The band structure of the clean Si(111)-(5×4) surface is essentially a folded version of the (5×2) surface with three occupied and three unoccupied surface states localized within the bulk gap region. For the Ca-covered Si(111)-(5×4) surface, there are four states within the gap region, three occupied and one unoccupied, with the lowest band gap occurring at the Γ point of the surface Brillouin zone.

As mentioned earlier, due to computational limitations we carried out the investigations of the (5×4) surface with a
smaller basis set (corresponding to the kinetic-energy cutoff of 8 Ryd). With this basis set we obtained the band-gap values of 0.28 and 0.15 eV for the clean and Ca-covered \((5 \times 4)\) surfaces, respectively. In order to compare these results with the corresponding results for the \((5 \times 2)\) reconstruction, it will be meaningful to scale these so that the band gap of the clean \((5 \times 4)\) matches with that for the clean \((5 \times 2)\). This would require a scale factor of 0.56/0.28 = 2. With this scaling we estimate the band gap of the Ca-covered \((5 \times 4)\) surface to be 0.30 eV. Thus we predict the band gap of the Ca-(\(5 \times 4)\) surface to be slightly smaller than the band gap of the Ca-(\(5 \times 2)\) surface. Applying a similar scaling to the density-of-states results shown in Fig. 3(c), we can infer that the energy difference between the highest occupied and lowest unoccupied surface peaks remains essentially the same for both Ca-(\(5 \times 4)\) and Ca-(\(5 \times 2)\) surfaces. From Fig. 3(c) we have identified three surface peaks within the bulk gap region. Two of these peaks, V1 and V2 in the valence-band region, are quite close to the two corresponding peaks on the \((5 \times 2)\) surface. The third peak, C1 at approximately \(E_c +0.5\) eV, can be easily related to the shoulderlike feature, C1, on the \((5 \times 2)\) surface.

In Fig. 9(b) we have attempted to compare our theoretical results with the angle-resolved measurements made by Sakamoto et al.,\textsuperscript{11} for the dispersion of low-binding-energy surface states along \(\Gamma-J\) (i.e., along the chain normal direction on the surface plane). For this comparison, we have to make suitable adjustments of our theoretical results. First of all, we will assume that the dispersion of the occupied surface states obtained with the low kinetic-energy cutoff of 8 Ryd will essentially be the same as with a larger basis set. Second, we will consider shifting our LDA results for unoccupied states by approximately 0.5 eV to match the \((5 \times 4)\) bulk band gap to the experimental band gap of approximately 1 eV. With this adjustment of unoccupied states, we then place the Fermi edge in the experimental results from Sakamoto et al. close to the "adjusted" lowest unoccupied state.

Sakamoto et al. employed two photon energies (17 and 21.2 eV) to examine the dispersion of surface states for Ca-(\(5 \times 4)\) along two azimuths: along and perpendicular to the Si chains. The use of these two photon energies has produced significant differences in the features in the angle-resolved photoemission spectra (ARPES). Such differences relate to both energy location as well as peak intensity of surface states. These differences may be taken as an indication that the mapped surface states are resonant with bulk states. Along the azimuth studied in the present work, we interpret the experimental results in terms of three surface bands with binding energy less than 2 eV. In Fig. 9(b) we have shown the experimental measurements obtained from both photon energies. The experimental results from the use of the two photon energies produce a common surface-state dispersion in the very low binding-energy range close to the bulk valence-band maximum. We interpret the experimental measurements in terms of three surface states. Our calculations confirm that all these states resonate with the bulk spectrum. After careful investigations of charge-density plots (not shown here), we have identified four slab bands that can be matched with the three surface states measured experimentally. This is done in Fig. 9(b).

Our partial charge-density plots in Figs. 9(c)(i)-(iv) clearly show that the highest occupied surface state \(S_1\) is localized along the buckled Si atoms forming the HCC chain. Moreover, the lowest unoccupied surface state \(S_2\) originates from the \(sp\) orbitals around the edges of the HCC chain. These orbital natures are quite similar to the corresponding features for the Ca-(\(5 \times 2)\) surface. We also present the total charge-density plot along different lines connecting the adsorbed Ca atoms with the Si atoms in both SZ and HCC chains. It is clearly seen that the total valence charge of the Ca atoms is transferred to the neighboring Si chain atoms. Figure 4(c) shows that more charge from Ca(B1) and Ca(D) are transferred to the Si atoms in the SZ chain, whereas Ca(C) and Ca(A1) transfer almost all of their valence charges to the HCC chain atoms. Ca(B2) and Ca(A2) transfer more charge to the HCC. Although all Ca atoms transfer their charge in a similar manner and extent, the charge transfers from Ca(A2) and Ca(D) show a hump feature, suggesting that these Ca atoms transfer their charge to more than one Si atom in the HCC.

We can compare charge transfer from Ca atoms to the Si chains for the \((5 \times 4)\) and \((5 \times 2)\) structures. The charge transfer from Ca(B) and Ca(C) remains the same for the two reconstructions. The formation of the \((5 \times 4)\) structure, characterized with two closely lying lines A and D, has resulted in some change in the charge transfer from Ca atoms in line A: while equal amounts of charge are transferred to both SZ and HCC for \((5 \times 2)\), there is more charge transfer to HCC for \((5 \times 4)\). The sum of charge transfer from the A and D lines in \((5 \times 4)\), however, is almost equally divided between the HCC and SZ chains. Therefore, it can be said that the role of charge transfer from the A and D lines in \((5 \times 4)\) is similar to the charge transfer from the A line in \((5 \times 2)\).

Our simulated scanning tunnel microscope (STM) images are shown in Fig. 5(c). For the negative bias of 2 eV (left panel of Fig. 5), both the SZ and HCC chains appear almost equally bright. For the positive bias of 2 eV (right panel of Fig. 5), the SZ chain appears a little brighter although the HCC chain also is quite bright. Clearly the STM images for the \((5 \times 4)\) structure are significantly different from the images for the \((5 \times 1)\) and \((5 \times 2)\) structures. Earlier we explained the difference in the images for the \((5 \times 1)\) and \((5 \times 2)\) structures to arise from the formation of a new Ca line \(C_\text{S}\), and in the reduction of concentration of Ca atoms in the other lines \(A\) and \(B\). The difference in the images for the \((5 \times 2)\) and \((5 \times 4)\) structures can similarly be explained in terms of the formation of an additional Ca line \(D\) for the latter structure.

D. Relative stabilities of reconstructions

As mentioned earlier Sakamoto et al.,\textsuperscript{10,11} concluded that the \((5 \times 2)\) and \((5 \times 4)\) reconstructions are stable while \((5 \times 1)\) is not. Using our theoretical method we can examine the relative stabilities of these reconstructions. As the Ca coverage is not the same for the three reconstructions, we express the surface formation energy of a \((5 \times n)\) reconstruction as

\[
\text{Formation Energy} = E_{\text{surf}} - nE_{\text{atom}}
\]
Ideal Surface of can be considered as a thermally induced disordered version where conclusion drawn by Sakamoto unfavorable stability of the stability of three reconstructions are expected to be stable. However, the two subregions. In subregion 1 Ewald energy. Subregion 2 range of the variable crystal.

$\Delta E_n = E_n - E_{ref} - \Delta N_Ca(\mu_{Ca\ bulk} - \mu_{Ca})$

$= E(5 \times n) - nE(5 \times 1) - \frac{2}{3}\mu_{Ca\ bulk} - \frac{2}{3}(\mu_{Ca} - \mu_{Ca\ bulk})$

$= E(5 \times n) - nE(5 \times 1) - \frac{2}{3}\mu_{Ca\ bulk} - \frac{2}{3}\Delta \mu,$

where $E_n$ is the total energy of the $(5 \times n)$ reconstruction, $E_{ref}$ is taken as the total energy of the clean Si(111)-(5x1) surface, and $\mu_{Ca\ bulk}$ is taken as the total energy of bulk fcc Ca crystal.

Figure 10 shows the results for the physically meaningful range of the variable $\Delta \mu$. We divide the Ca-rich region into two subregions. In subregion 1 (indicated as region 1) all the three reconstructions are expected to be stable. However, the stability of $(5 \times 1)$ is rather marginal and thus supports the conclusion drawn by Sakamoto et al. that this reconstruction can be considered as a thermally induced disordered version of $(5 \times 2)$. An inspection of various terms making up the total energy suggests that the largest contribution toward the unfavorable stability of the $(5 \times 1)$ reconstruction is the Ewald energy. Subregion 2 (indicated as region 2) shows that in this range of Ca richness, $(5 \times 4)$ is clearly the most stable structure with $(5 \times 2)$ being only marginally stable. Surprisingly, for very poor and unpractical Ca chemical-potential region (indicated as region 3), the $(5 \times 1)$ reconstruction tends to be more stable than the other two reconstructions.

**IV. SUMMARY AND CONCLUSION**

We have determined the atomic geometry and electronic structure of the recently proposed $(5 \times 1)$, $(5 \times 2)$, and $(5 \times 4)$ reconstructions of the Si(111) surface upon adsorption of 0.4, 0.3, and 0.3 ML of Ca atoms, respectively. The structural models are based on a combination of the Seiwatz (SZ) and the honeycomb channel (HCC) chains of Si atoms. It is shown that, in Ca-rich conditions, the $(5 \times 1)$ reconstruction is at best marginally stable and $(5 \times 4)$ is the most stable configuration. The adsorption of the Ca lines pushes the Si chain layer toward the first Si(111) layer. The Ca atoms are adsorbed at different heights for the three reconstructions. For the $(5 \times 1)$ reconstruction, the two Ca lines, $A$ and $B$, are at the same height, and the shortest distance between Ca and Si atoms is 3.06 Å. For the $(5 \times 2)$ reconstruction, the Ca adatoms reside at different heights: the $A$ and $B$ lines are at one height and, the $C$ line lies higher. The maximum Ca-Ca separation is 0.17 Å and the shortest Ca-Si distance is 2.38 Å. For the $(5 \times 4)$ reconstruction, the Ca adatoms reside at different heights. The $A$ line shows a huge vertical buckling of 0.89 Å, and the vertical heights of the lines $B$, $C$, and $D$ are determined to lie within this buckling range. The shortest Ca-Si distance is 2.45 Å.

All the three reconstructions are found to be semiconducting with surface band gap smaller than the bulk direct band gap. This behavior is contributed by charge transfer from Ca atoms to their neighboring atoms in the Si chain layer. These surface reconstructions lead to at least three identifiable peaks in the density of states within about 2.0 eV around the bulk band-gap region. The highest occupied state originates from the topmost Si atoms forming the SZ chain. Simulated STM images suggest that for the $(5 \times 2)$ structure, the SZ chain is brighter under negative bias and the HCC chain is brighter under positive bias. For the $(5 \times 4)$ structure, both the HCC and SZ chains illuminate almost equally for negative bias and the SZ chain illuminates slightly brighter for positive bias.

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FIG. 10. (Color online) Relative surface formation energy per $(1 \times 1)$ unit cell for Ca/Si(111)-(5x$n$) surfaces plotted as a function of the Ca chemical potential.