La induced Si$_3$ trimer monolayer on Si(111) surface: an \textit{ab initio} study

Guang Yang$^{1,2}$, Jun-Shuai Chai$^{1,3}$, Li-Fang Xu$^{1,4,}$ and Jian-Tao Wang$^{1,2,4,}$

$^1$ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
$^2$ School of Physics Sciences, University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China
$^3$ Key Laboratory of Microelectronics and Integrated Technology, Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, People’s Republic of China
$^4$ Songshan Lake Materials Laboratory, Dongguan 523808, Guangdong, People’s Republic of China

* Authors to whom any correspondence should be addressed.
E-mail: wjt@aphy.iphy.ac.cn and lfxu@iphy.ac.cn

Keywords: Si(111) surface, Si$_3$ trimer, electronic property, \textit{ab initio} calculation

Abstract

The $\pi$-bond Seiwatz chain (SC) is one of the well-known reconstruction induced by alkaline or rare earth metals on Si(111) surface. Here we identify by \textit{ab initio} calculations a new reconstruction of La induced quasi-two-dimensional Si$_3$ trimer monolayer on Si(111)-$(\sqrt{3} \times \sqrt{3})R30^\circ$ surface. Its surface unit cell has one La atom and one Si$_3$ trimer with the same La coverage (1/3 monolayer) as SC structure and the Si$_3$ trimer satisfies the electron counting rule with a transfer of valence electrons from La atom, formally as La$_3^{+} [\text{Si}^-$]$_3$, in correspondence to the \textit{milkstool} model for Bi trimers on Si(111) surface. Band structure calculations show a semiconducting character with an indirect surface band gap of 0.76 eV. Moreover, a two-stage conversion process between the Si$_3$ trimer and SC structure is verified by the climbing-image nudged elastic band method. These findings pave the way for further exploration of the new surface structure and its outstanding properties.

1. Introduction

Self-organized ordered nanostructures with identical size on semiconductor surfaces have aroused great interest, because of the potential of fabricating nanometer-scale electronic devices [1–5]. By changing the coverage of metal atoms and the growth temperature, one-dimensional (1D) or two-dimensional (2D) nanostructures can be formed with novel electronic properties [6–21]. For alkaline earth metal (AEM = Ca, Sr, Ba) on Si(111) surface, aligned honeycomb-chain-channel (HCC) [22–25] and $\pi$-bond Seiwatz chain (SC) [26–28] are the two basis building blocks, and the AEM adatoms are located in the channels separated by the honeycomb or Seiwatz Si chains. The observed AEM/Si(111) reconstructions satisfy a simple electron counting rule (ECR): each AEM atom donates two electrons to stabilize the (3 $\times$ 2) HCC or (2 $\times$ 1) SC unit [22, 29, 30].

For rare earth metal (REM) on Si(111) surface, there are two kinds of chemical valence states, +2 valence state for Sm, Eu, Yb [31–33] and +3 valence state for La, Ce, Er, Dy, Th, Ho [34–42], respectively. Divalent REM atoms can induce HCC structure on (3 $\times$ 2) surface at the lowest coverage of 1/6 monolayer (ML) [25, 30, 43–45] and SC structure on (2 $\times$ 1) surface at the highest coverage of 1/2 ML [46], as well as the mixed HCC + SC structure on Si(111)-(5 $\times$ k) ($k = 2, 4$) surface at the intermediate coverage [47, 48]. Meanwhile, trivalent REM such as La on Si(111) surface can induce (5 $\times$ 2) HCC + SC, (2m + 1) $\times$ 6 (m > 2) HCC + SC or (2 $\times$ 3) SC structure [41, 42] with the change of La atom coverage. Particularly, in La induced Si(111)-(2 $\times$ 3) SC surface structure at 1/3 ML coverage, each La atom donates three electrons to saturate the dangling bonds of Si atom chains [41, 42].

In this paper, we report by \textit{ab initio} calculations a new reconstruction of La induced quasi-2D Si$_3$ trimer monolayer on Si(111)-$(\sqrt{3} \times \sqrt{3})R30^\circ$ surface. This La–Si$_3$ structure has a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface unit...
cell with one La atom and one Si$_3$ trimer, and the Si$_3$ trimer satisfies the ECR with a transfer of valence electrons from La atoms, formally as La$^{3+}$[Si$_3^-$]$_n$, in correspondence to the milkstool structure for Bi and Sb trimers on Si(111) surface [17–21]. Electronic band structure calculations show that this Si$_3$ trimer structure has a semiconducting character with an indirect surface band gap of 0.76 eV. Ab initio molecular dynamics simulations demonstrate that Si$_3$ trimer structure can be derived from SC structure at high temperature. Moreover, a two-stage conversion pathway between these two structures is verified by the climbing-image nudged elastic band method.

2. Computational method

Our density functional theory calculations are performed using the Vienna ab initio simulation package (VASP) [49, 50] with the projected augmented wave potential [51, 52]. The generalized gradient approximation developed by Perdew–Burke–Ernzerhof is used to treat the exchange and correlation functional [53]. The valence states 3$s^2$3$p^6$ for Si and 5$s^2$5$p^6$5$d^1$6$s^2$ for La are used with an energy cutoff of 500 eV for the plane-wave basis set. A supercell $XYZ = 6.65 \times 6.65 \times 42.73$ Å with a $(\sqrt{3} \times \sqrt{3})R\bar{3}0^\circ$ periodic lattice is used to simulate the surface structure. There are six Si layers with a vacuum region of $\sim 2.0$ Å in the Z direction. The dangling bonds of the lowest Si layer are passivated by hydrogen atoms. The Brillouin zone is sampled using the Monkhorst–Pack scheme [54] with a $9 \times 9 \times 1 \Gamma^\star$-centered $k$ grid. Throughout the calculations, three bottom Si layers are fixed, while other atoms are fully relaxed. The energy minimization is done over the atomic and electronic degrees of freedom using the conjugate gradient iterative technique. The convergence criteria of electronic self-consistent is set to $10^{-4}$ eV for total energy.

3. Results and discussion

3.1. Structural stability

We first characterize the La induced Si$_3$ trimer monolayer structure on Si(111)-(\(\sqrt{3} \times \sqrt{3})R30^\circ\) surface. This La–Si$_3$ structure has a $\sqrt{3} \times \sqrt{3}$ surface unit cell (black solid lines in figure 1(a)) with one La atom and one Si$_3$ trimer (red spheres) and such Si$_3$ trimers satisfy the ECR with a transfer of valence electrons from La atoms, formally as La$^{3+}$[Si$_3^-$]$_n$, in correspondence to the milkstool structure for Bi and Sb trimers on Si(111) surface [17–21]. Like as Bi trimer on Si(111) surface [19], each Si$_3$ trimer is located on the $T_4$ site with a Si–Si bond length of 2.44 Å. Meanwhile, each Si atom in trimer is bonded to substrate Si atom with almost same bond length of 2.45 Å. The bond length between La and its nearest neighboring Si in trimer is 2.98 Å. It is worth noting that La atom is located on another $T_4$ site and has the same height with Si$_3$ trimer (see the side view in figure 1(b)). For comparison, the SC reconstruction on Si(111)-(2 $\times$ 3) surface is shown in figures 1(c) and (d). In the unit cell, two La atoms are located on the $T_4$ and $H_3$ site, respectively, and six surface Si atoms (red spheres) form a Si atom chain along [100] orientation. The unit cell of SC structure is as twice as large Si$_3$ trimer structure and both Si$_3$ trimer and SC structures have the same La and Si atom density on Si(111) surface. Total energy calculations show that SC is slightly lower than Si$_3$ trimer with an energy difference of 43 meV per LaSi$_3$ unit, suggesting the stability for both structures are very close. It is worth noted that these SC and Si$_3$ trimer structures have a low La coverage of 1/3 ML, and at high La coverage of 2/3 ML, a Si$_3$ trimer bilayer structure might be formed on the Si(111) surface [55].

To examine the thermal stability of this new Si$_3$ trimer monolayer structure, we have further performed ab initio molecular dynamics (AIMD) simulations with the canonical (NVT) ensemble at a temperature of 300 K, using the Nosé thermostat [56] with a step of 1 fs. We rebuild the $2\sqrt{3} \times 3$ supercell (\(XYZ = 13.3 \times 11.52 \times 50.46\) Å) containing four La atoms and twelve surface Si atoms on Si(111) substrate. The energy fluctuations for Si$_3$ trimer on Si(111) surface are plotted in figure 2. The initial structure at step 0 and final structure at step 8000 are also given in insets of figure 2, respectively. It is shown that after running 8 ps at 300 K, the Si$_3$ trimer structure can keep well. The La atoms and Si$_3$ trimers deviate from the equilibrium positions ($T_4$ site) slightly, but they can be relaxed back to the initial positions, suggesting robust stability of Si$_3$ trimer structure at room temperature.

3.2. Surface electronic properties

Figure 3(a) presents the two-dimensional electron localization function (2D ELF) map across the Si$_3$ trimer monolayer section on Si(111)-(\(\sqrt{3} \times \sqrt{3})\) surface with a range from 0.2 to 0.8. The ELF = 0 or ELF = 1 represent the complete delocalization or localization of electrons [57–59], respectively. 2D ELF shows that the electrons are predominantly localized on Si atoms of trimer and few localized around La atom. This
Figure 1. (a) Top view and (b) side view for La induced Si$_3$ trimer monolayer structure on Si(111)-(\(\sqrt{3} \times \sqrt{3}\))R30° surface. (c) Top view and (d) side view for La induced SC structure on Si(111)-(2 \times 3) surface. The green, red, and blue spheres represent La, surface and deeper Si of the Si(111) surface, respectively. Black solid lines represent \(\sqrt{3} \times \sqrt{3}\)-R30° unit cell for Si$_3$ trimer structure and 2 \times 3 unit cell for SC structure. Black dotted lines represent \(\sqrt{3} \times 3\) supercell.

Figure 2. Energy fluctuation of Si$_3$ trimer monolayer structure in AIMD simulations at 300 K running 8000 fs. The insets show the corresponding top view of Si$_3$ trimer structure for initial structure (left) and final structure (right) during the simulation, respectively.

means that a number of electrons transfer from La atoms to surrounding Si atoms of trimer. Thus, the ELF maps demonstrate an ionic bonding feature between La and its nearest-neighbor Si trimer.

The calculated electronic band structures for Si$_3$ trimer monolayer structure is plotted in figure 3(b), where the valence band maximum (VBM) is located at \(\Gamma\) point and the conduction band minimum (CBM) is located at \(K\) point, respectively, showing a semiconducting feature with an indirect band gap of 0.76 eV. The band gap reflects Si$_3$ trimer structure satisfying the ECR in La$^{3+}[\text{Si}^-]_3$ form. Such electronic band structure property is analogous to that of Bi$_3$ trimer on Si(111) surface with an indirect band gap of 0.45 eV [21]. We can see that this new Si$_3$ trimer monolayer structure with a low La coverage of 1/3 monolayer satisfies the ECR and has a larger band gap of 0.76 eV. However, at high 2/3 ML La coverage, Si$_3$ trimer
bilayer structure has a small surface band gap of 42 meV, where two La atoms have different valence states, \( \text{La}^{2+} \) and \( \text{La}^{3+} \) [55].

To clarify the atomic origin of the bands near the Fermi energy level (\( E_F \)), the band-decomposed charge density distributions (BDCDDs) for the lowest conduction band (CB1) and the highest valence band (VB1) of Si3 trimer structure are calculated, as shown in figures 3(c) and (d). The CB1 band is mainly contributed by La atoms (see figure 3(c)), while the VB1 band is mainly contributed by Si3 trimers (see figure 3(d)), suggesting that CB1 and VB1 are two surface bands. Therefore, the BDCDDs pictures indicate that CB1 is empty state contributed by La atom and VB1 is full state contributed by surface Si3 trimer, which is consistent with ELF results in figure 3(a).

We have further simulated the scanning tunneling microscope (STM) images of Si3 trimer structure. Figure 3(e) shows the image of empty-state with a bias of +1.8 V, where the bright honeycomb protrusions reflect La atoms; while figure 3(f) shows the image of filled-state with a bias of −1.8 V, where the bright trimer protrusions reflect surface Si3 trimers. These STM images are in agreement with the calculated BDCDDs results. Moreover, our simulated STM image in figure 3(f) looks alike to the reported STM images of Bi trimers on Si(111) surface [21] due to they have similar valance states.

### 3.3. Structure conversion pathway

We finally examine the kinetic conversion pathway at the atomic scale between SC and Si3 trimer structures using the climbing-image nudged elastic band (CI-NEB) method [60, 61] implemented in VASP. To simulate structural transition state, we use a supercell \( XYZ = 6.65 \, \text{Å} \times 11.52 \, \text{Å} \times 50.46 \, \text{Å} \) with a \( \sqrt{3} \times 3 \) periodic lattice (marked as black dotted lines in figures 1(a) and (c)), which ensures the same number of atoms for both Si3 trimer and SC structure (see figure 4(b)). The \( k \)-point sampling of \( 5 \times 3 \times 1 \) is used. Throughout the CI-NEB calculations, the energy convergent criterion is \( 10^{-4} \) per supercell, and the forces on all relaxed atoms are less than 0.05 eV Å\(^{-1}\).

The relative total energy along the path from SC structure toward Si3 trimer structure is plotted in figure 4(a). The key structural snapshots along the pathway at step 0, 10, 19, 28 and 38 are given in figure 4(b). It is verified a two-stage conversion process between the Si3 trimer and SC structures. At the first stage, from step 0 to step 10, the relative total energy initially increases due to the bond breaking between Si1–Si6 and Si2–Si4 atoms; from step 10 to step 19, the relative total energy obviously decreases owing to bond rebonding between Si1–Si2 and Si4–Si6 atoms, forming Si-123 trimer and Si-456 trimer. As a result, the quasi-1D SC structure is broken and a quasi-2D intermediate structure is formed. For this intermediate structure, Si-123 trimer and La(I) atoms are located on the H3 site, and Si-456 trimer and La(II) atoms are located on the T4 site, respectively. The corresponding conversion barrier is estimated to be 0.58 eV per \( \sqrt{3} \times \sqrt{3} \) unit cell (with one La atom and three surface Si atoms). This low kinetic barrier
suggests that the Si–Si bond breaking and rebonding can easily take place. However, the intermediate structure is very unstable due to Si-123 trimer and La(I) atoms are located on the unfavorable H₃ site.

At the second stage, from step 19 to step 28, the relative total energy again increases due to the atomic shifting of La(I) atom and bond breaking between Si₂, Si₃ and substrate Si atoms (blue spheres) with Si-123 trimer anticlockwise whirling; from step 28 to step 38, the relative total energy decreases owing to atomic shifting of La(I) atom and bond rebonding between Si₂, Si₃ and substrate Si atoms with Si-123 trimer anticlockwise whirling. In this stage, Si-123 trimer rotates anticlockwise from H₃ site toward T₄ site and La(I) atom basically moves linearly shifting from H₃ toward T₄ site, while Si-456 trimer and La(II) atoms are basically stock-still at T₄ site. The corresponding conversion barrier is estimated to be 0.33 eV, suggests that structure transition can easily take place. As a result, Si₃ trimer structure is obtained from SC structure via a two-stage conversion process. On the contrary, the structure transition from Si₃ trimer structure to SC structure is more difficult with a larger energy barrier of 0.64 eV.

To examine the thermal stability of SC structure and the possible structure transition from SC toward Si₃ trimer, we have further carried out AIMD simulations with the canonical (NVT) ensemble using the Nosé thermostat [56] with a step of 1 fs at temperature of 300 K and 900 K, respectively. The energy
fluctuations for SC structure on Si(111) surface are plotted in figure 5(a) at 300 K and figure 5(b) at 900 K, respectively. At room temperature (300 K), the SC structural energy fluctuations are very small and geometry remains intact on the whole. With the temperature increasing up to 900 K, as shown in figure 5(b), the SC structure can convert to Si3 trimer structure gradually. These results suggest that the SC structure is stable at room temperature and structure transition from SC structure to Si3 trimer structure will undergo spontaneously at high temperature. Based on our MD simulations, we can see that this new Si3 trimer structure can be derived from SC structure at high temperature, and once Si3 trimer structure is formed, it can be kept at room temperature as shown in figure 2.

4. Summary

In summary, we have identified a new La induced Si3 trimer monolayer reconstruction on Si(111)- (√3 × √3)R30° surface with 1/3 ML La coverage and systematically studied its structural stability and electronic properties. In each √3 × √3 unit cell, Si3 trimer satisfies the ECR with a transfer of valence electrons from La atom, formally as La3+[Si−]3. Electronic band structure calculations show that this Si3 structure has a semiconducting character with an indirect surface band gap of 0.76 eV. Ab initio molecular dynamics simulations demonstrate that Si3 trimer structure can be derived from SC structure at high temperature. Our results suggest that Si3 trimer structure as well as SC structure can be formed on Si(111) surface due to their small energy difference and low conversion barrier between them. These results provide a new surface structure and expand our understandings for the REM induced reconstruction on Si(111) surface.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 11974387), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB33000000), and the National Key Research and Development Program of China (Grant No. 2020YFA0711502).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Jian-Tao Wang https://orcid.org/0000-0002-0786-1212

References

[1] Desjonqueres M C and Spanjaard D 2012 Concepts in Surface Physics (Berlin: Springer)
[2] Cho J H, Lee J Y and Kleinman L 2005 Phys. Rev. B 71 081310(R)
[3] Erwin S C, Barke I and Himpsel F J 2009 Phys. Rev. B 80 155409
[4] Riikonen S and Sánchez-Portal D 2005 Phys. Rev. B 71 235423
[5] Schmidt W G, Babilon M, Thierfelder C, Sanna S and Wippermann S 2011 Phys. Rev. B 84 115416
[6] Boshart M A, Bailes A A and Seiberling I E 1996 Phys. Rev. Lett. 77 1087
[7] Yeom H W et al 1999 Phys. Rev. Lett. 82 4898
[8] Li J L et al 2002 Phys. Rev. Lett. 88 066101
[9] Owen J H G, Miki K, Koh H, Yeom H W and Bowler D R 2002 Phys. Rev. Lett. 88 226104
[10] Wu K et al 2003 Phys. Rev. Lett. 91 126101
[11] Portavoce A, Berbezier I and Ronda A 2004 Phys. Rev. B 69 155416
[12] Wang J-T, Wang E G, Wang D S, Mizuseki H, Kawazoe Y, Naitoh M and Nishigaki S 2005 Phys. Rev. Lett. 94 226103
[13] Zhang C, Chen G, Wang K, Yang H, Su T, Chan C T, Loy M M T and Xiao X 2005 Phys. Rev. Lett. 94 176104
[14] Theberge F, Liu W, Simard P T, Becker A and Chin S L 2006 Phys. Rev. E 74 036406
[15] Stekolnikov A A, Bechstedt F, Wisniewski M, Schäfer J and Claessen R 2008 Phys. Rev. Lett. 100 196101
[16] Niu C-Y, Wang J-T, Wang E and Chen C 2013 J. Chem. Phys. 138 164705
[17] Mårtensson P, Meyer G, Amer N M, Kaxiras E and Pandey K C 1990 Phys. Rev. B 42 47230
[18] Woicik J C, Kendelewicz T, Miyano K E, Bouldin C E, Meissner P L, Pianetta P and Spicer W E 1991 Phys. Rev. B 43 4331
[19] Miwa R H, Schmidt T M and Srivastava G P 2003 J. Phys.: Condens. Matter. 15 2441
[20] Zhu X-G et al 2013 Surf. Sci. 618 115
[21] Chi L, Nogami J and Singh C V 2021 Phys. Rev. B 103 075405
[22] Erwin S C and Weitering H H 1998 Phys. Rev. Lett. 81 2296
[23] Kang M-H, Kang J-H and Jeong S 1998 Phys. Rev. B 58 R13359
[24] Lottermoser L et al 1998 Phys. Rev. Lett. 80 3980
[25] Chai J-S, Li Z-Z, Xu L-F and Wang J-T 2018 Phys. Chem. Chem. Phys. 20 25235
[26] Quinn J and Jona F 1991 Surf. Sci. 249 L307
[27] Kubo O, Sararin A A, Zotov A V, Ryu J-T, Tani H, Harada T, Katayama M, Lifshits V G and Oura K 1998 Surf. Sci. 415 L971
[28] Seiwatz R 1964 Surf. Sci. 2 473
[29] Battaglia C, Cercellier H, Monney C, Garnier M G and Aebi P 2007 Europhys. Lett. 77 36003
[30] Lee G, Hong S, Kim H, Shin D, Koo J Y, Lee H I and Moon D W 2001 Phys. Rev. Lett. 87 056104
[31] Kuzmin M, Vaara R-L, Laukkanen P, Perälä R E and Väyrynen I J 2003 Surf. Sci. 538 124
[32] Ehret E, Palmino F, Mansour L, Duverger E and Labrune J-C 2004 Surf. Sci. 569 23
[33] Saranin A A, Zotov A V, Pisarenko I V, Lifshits V G, Katayama M and Oura K 2004 Japan. J. Appl. Phys. 43 1110
[34] Perkins E W, Scott I M and Tear S P 2005 Surf. Sci. 578 80
[35] Engelhardt I, Preinesberger C, Becker S K, Eisele H and Dähne M 2006 Surf. Sci. 600 755
[36] Franz M, Große J, Kohlhaas R and Dähne M 2015 Surf. Sci. 637–638 149
[37] Liu L, Lin Z, Wang Y, Wang W, Yang F, Zhu X and Guo J 2018 Surf. Sci. 674 40
[38] Tayran C 2019 Surf. Sci. 653 222
[39] Sakamoto K, Zhang H M and Uhrberg R I G 2003 Phys. Rev. B 68 245316
[40] Sakamoto K, Pick A and Uhrberg R I G 2005 Phys. Rev. B 72 195342
[41] Kresse G and Hafner J 1993 Phys. Rev. B 47 558
[42] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[43] Blöchl P E 1994 Phys. Rev. B 50 17953
[44] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[45] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[46] Perdew J P and Wang Y 1992 Phys. Rev. B 45 13244
[47] Chai J-S, Yang G, Xu J, Wang W-W, Xu L-F and Wang J-T 2021 Phys. Chem. Chem. Phys. 23 11466
[48] Nosé S 1984 J. Chem. Phys. 81 511
[49] Becke A D and Edgecombe K E 1990 J. Chem. Phys. 92 5397
[50] Savin A, Jepsen O, Flad J, Andersen O K, Preuss H and von Schnering H G 1992 Angew. Chem., Int. Ed. Engl. 31 187
[51] Silvi B and Savin A 1994 Nature 371 683
[52] Henkelman G, Uberuaga B P and Jónsson H 2000 J. Chem. Phys. 113 9901
[53] Henkelman G and Jürgen H 2000 J. Chem. Phys. 113 9978