First-principles investigation of the Ca/Si(111)2×1 surface

Sukmin Jeong
Department of Physics and Institute of Photonics and Information Technology, Chonbuk National University, Chonju 561-756, Korea

Ji Young Lee and Myung Ho Kang*
Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea
(Received 25 July 2005; revised manuscript received 30 September 2005; published 23 November 2005)

Atomic and electronic structure of the Ca/Si(111)2×1 surface has been studied by density functional theory calculations. The Seiwatz chain structure with Ca adsorbed on the T_4 site, suggested in previous experiments, is found to be the most stable among the structural models considered. This Seiwatz-T_4 model produces a semiconducting surface band structure: Two filled and one empty surface-state bands are found in the gap originating from the Si dangling-bond states on the Seiwatz chain and the Ca 4*s* states, respectively, which indicates a complete charge transfer from Ca to the Si surface. The calculated band dispersions agree well with photoemission data, but the simulated scanning tunneling microscopy images, empty-state images of bright stripes representing the one-dimensional Ca chains, and filled-state images of hexagonal lobes representing the Si dangling bonds, partly differ from experimental images of only bright stripes for both empty and filled states.

DOI: 10.1103/PhysRevB.72.193309 PACS number(s): 68.43.Bc, 73.20.At, 68.37.Ef

One-dimensional (1D) chain structures of metal atoms grown on the Si(111) surface have been extensively studied in connection with a realization of 1D atomic metal wires, an issue of growing importance both for academic interest in exotic electronic properties and for applications in nanotechnology. Representative systems include alkali-metal (AM)/Si(111)3×1,[1–5] alkali-earth-metal (AEM)/Si(111)3×2,[6–8] In/Si(111)4×1,[9–11] and Au/Si(111)5×2.[12–15] Of particular interest is the Ca adsorbed Si(111) surface, which is known to form a series of 1D chain structures with Ca coverage:[16–18] The lowest-coverage 3×2 phase, the intermediate $n\times2$ phases ($n=5,7$, and 9), and the highest-coverage 2×1 phase. Many efforts have been focused on the 3×2 and 2×1 phases, since they were suggested to serve as two building units of the other higher-order $n\times2$ phases.[16–18] While a solid picture of the atomic and electronic structure has been established for the lowest-coverage 3×2 phase[8,17–22] based on the knowledge obtained for the extensively studied AM/Si(111)3×1 surface,[2–5] our understanding of the highest-coverage 2×1 phase is not yet solid, although it belongs to the simplest Si(111) systems with a small unit cell and a known adsorbate coverage.

Previously, Baski *et al.*[16] and Sekiguchi *et al.*[17] obtained scanning-tunneling microscopy (STM) images for Ca/Si(111)2×1 that display well-ordered 1D chain structures along the $[1\bar{1}0]$ direction and suggested a structural model where Ca atoms form 1D atomic chains embedded between π-bonded Seiwatz chains of the reconstructed Si(111)2×1 surface (see Fig. 1). In view of the divalency of Ca, this Seiwatz chain model is a plausible 2×1 version of the honeycomb chain model for the AM/Si(111)3×1 surfaces,[4,5] and was found to be compatible with Si 2*p* surface core-level shift measurements.[16,18] In their recent angle-resolved photoemission spectroscopy (ARPES) studies, Kim *et al.*[21] and Sakamoto *et al.*[23] reported a semiconducting surface band structure for Ca/Si(111)2×1 and, by comparing with the calculated band structure of the clean Si(111)2×1 surface based on Seiwatz chains,[24,25] suggested a presence of Seiwatz chains in the Ca/Si(111)2×1 surface. However, such comparison with the clean surface containing Seiwatz chains is questionable because the electronic structure of a clean surface could be affected significantly due to a structural change induced by adsorption. So far, the experimentally proposed Seiwatz chain model for Ca/Si(111)2×1 has not been confirmed by direct measurements or by first-principles energetics calculations, and it remains to be examined if the Seiwatz chain model can reproduce the experimental electronic structures reported by ARPES and STM.

In this paper, we theoretically investigate the atomic and electronic structure of the Ca/Si(111)2×1 surface with emphasis on the experimentally proposed Seiwatz chain model. Our density functional theory calculations show that the Seiwatz chain structure with Ca on the T_4 site is energetically more stable than other models examined and produces a semiconducting band structure that explains well the dispersions and the atomic origins of ARPES surface-state bands. Our STM simulation for the Seiwatz-T_4 structure results in empty-state images of bright stripes and filled-state images of hexagonal lobes, partly disagreeing with experimental images of only stripes for both empty and filled states.

Density functional theory calculations have been performed using the generalized-gradient approximation[26] for exchange and correlation and the norm-conserving pseudopotentials[27,28] for ionic potentials. The Si(111) surface is simulated by a repeated slab geometry. Each unit cell consists of a slab of six Si layers and a vacuum region equivalent to six atomic layers. Ca is adsorbed on the top side of the slab, and the bottom is saturated by hydrogen atoms. The electronic wave functions are expanded into plane waves up to a kinetic energy of 15 Ry. Brillouin-zone integrations are done with a $(4\times8\times1)$ *k* point mesh for the 2×1 surface unit cell. The geometry optimization is done for all atoms

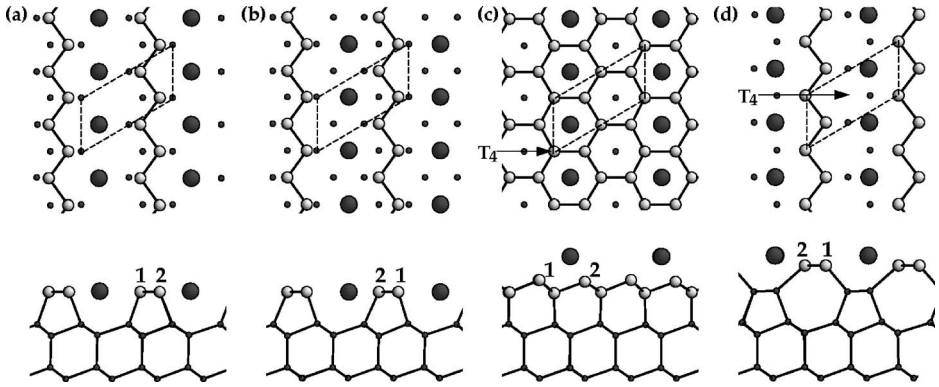

FIG. 1. Equilibrium geometries of the structural models for Ca/Si(111)2×1: (a) Seiwatz chain (T_4), (b) Seiwatz chain (H_3), (c) Overlayer (H_3), and (d) Pandey chain (H_3). The largest circles represent Ca atoms.

except for the two bottom-most Si layers until the remaining force acting on each ion is less than 0.05 eV/Å. Similar computational parameters were found to result in sufficiently converged energetics and structural properties in previous studies.[5,8,16]

Three structural models are considered for the Ca/Si(111)2×1 surface (see Fig. 1): The experimental Seiwatz chain model is energetically compared with the overlayer model and the Pandey chain model, where 1D chains of Ca atoms are adsorbed on the bulk-terminated Si(111)2×1 surface and on the reconstructed surface containing π-bonded Pandey chains, respectively. Two different adsorption sites T_4 and H_3 are examined for each model, and the coverage of Ca is assumed to be 0.5 monolayer (i.e., one Ca atom per 2×1 unit cell) based on experimental results.[16–18,21,23] For comparison of adsorption energetics between two models containing different numbers of substrate atoms, we calculate the relative surface formation energies given by $\Delta E_s = \Delta E_{\mathrm{tot}} - \Delta N_{\mathrm{Si}} \times \mu_{\mathrm{Si}}$. ΔE_{tot} and ΔN_{Si} represent the differences in total energy and in number of Si atoms, respectively, between the models. μ_{Si} is the chemical potential for Si atoms, here assumed to be in equilibrium with bulk Si.

We show the energy minimum structures for the three models in Fig. 1 and summarize their formation energies and optimized structural parameters in Table I.The Seiwatz chain model is far more stable than the others. Within the Seiwatz chain model the T_4 site is more favored over the H_3 site, but a relatively small energy difference of 0.09 eV enforces that the adsorption on the H_3 site should also be considered in the electronic structure investigation. Noticeable in the Seiwatz-T_4 structure is the unbuckled configuration of the Seiwatz chain, contrasting to a large buckling predicted for the clean Seiwatz chain surface.[24] In our calculations, the buckling ($\Delta z = 0.66$ Å) of the Seiwatz chain in the clean surface is completely eliminated (as $\Delta z < 0.01$ Å) upon Ca adsorption. The cause of this structural change and its effect on the surface electronic structure will be discussed shortly.

Figure 2 shows the surface band structures of the Seiwatz-T_4 and -H_3 models for Ca/Si(111)2×1. Both models produce similar semiconducting band structures. There are three noticeable surface-state bands in the gap, one empty and two filled bands. In their ARPES experiment, Sakamoto *et al.*[23] found two surface-state bands around the Fermi level (solid lines in Fig. 2): one dispersionless band (S_1') extended over the whole Brillouin zone and the other weaker feature (S_2')noticeable only near the $\bar{J}'$ point. The S_1' band was also reported in the work of Kim *et al.*,[21] as denoted by dashed line. As seen in Fig. 2(a), the filled states of the Seiwatz-T_4 model are in good agreement with the measured S_1' and S_2'. On the other hand, the Seiwatz-H_3 model shows a noticeable band splitting near $\bar{J}$, deviating from the measured ones. The present spectroscopic examination thus prefers the Seiwatz-T_4 model and figures out that the ARPES data near $\bar{J}$ represent two nearly degenerate surface-state bands.

In order to clarify the atomic origins of the surface band structure, we examine in Fig. 3 the charge characters of representative surface states for the Seiwatz-T_4 structure. As shown in Fig. 3(c), the two filled states, S_1 and S_2, represent the localized dangling bonds of the Si atoms in the Seiwatz chain and the empty state S_4, the delocalized 4*s* state of Ca. The stable σ bond along the Seiwatz chain also appears as a weak surface state (S_3) near $\bar{J}'$. In previous studies[21,23] the calculated band structure of the clean Si(111)2×1 surface with buckled Seiwatz chains[24] was used for comparison with ARPES data for Ca/Si(111)2×1. This comparison, however, is not appropriate since the Seiwatz chain structure changes upon Ca adsorption from a buckled to unbuckled configuration as mentioned before. In fact, as shown in Fig. 3(a), the dangling-bond states of the unbuckled Seiwatz chain are compared better with the filled bands (represented by S1 and S2) of Ca/Si(111)2×1 than those of the buckled

TABLE I. Formation energies and optimized structural parameters of the structural models for Ca/Si(111)2×1. Si_1 and Si_2 represent the topmost Si atoms denoted as 1 and 2 in Fig. 1. *z* and *d* represent the height difference and the distance, respectively, between given atoms. The formation energies are in electron volts/(2×1) relative to that of the Seiwatz chain (T_4) model. The lengths are given in angstroms. The calculated Si-Si bulk bond length is 2.37 Å.

	ΔE_s	$z_{\mathrm{Ca\text{-}Si}_1}$	$d_{\mathrm{Ca\text{-}Si}_1}$	$d_{\mathrm{Ca\text{-}Si}_2}$	$d_{\mathrm{Si}_1\text{-}\mathrm{Si}_2}$
Seiwatz chain (T_4)	0.00	0.07	3.05	2.95	2.41
Seiwatz chain (H_3)	0.09	0.01	3.04	2.97	2.41
Overlayer (H_3)	0.44	1.69	2.85	2.89	
Overlayer (T_4)	0.59	2.04	3.01	2.94	
Pandey chain (H_3)	0.91	0.69	3.20	2.97	2.42
Pandey chain (T_4)	0.92	0.71	2.97	3.19	2.42

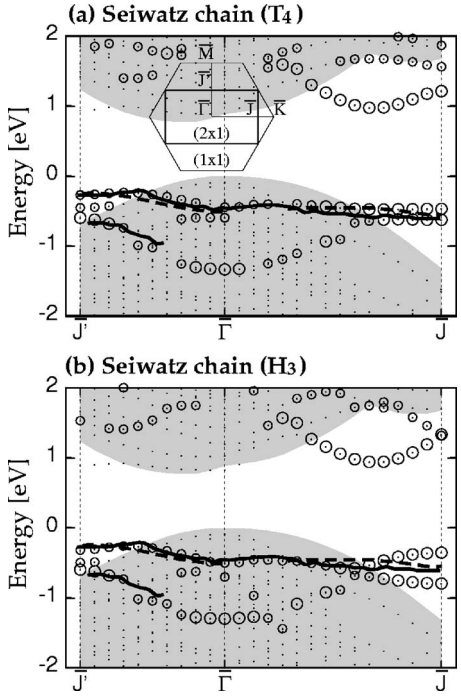

FIG. 2. Surface band structures of Ca/Si(111)2×1: (a) Seiwatz chain (T_4) and (b) Seiwatz chain (H_3). Shaded areas represent the projected bulk band structure. All energies are given relative to the valence-band maximum at $\bar{\Gamma}$. Large and small open circles represent the surface localized states containing more than 60% and 40%, respectively, of charge in the outermost two Si layers and the adsorbates (here, a thicker slab of 12 Si layers was employed for accurate surface-state resolution). Solid and dashed lines represent measured ARPES bands reported in Refs. 23 and 21, respectively.

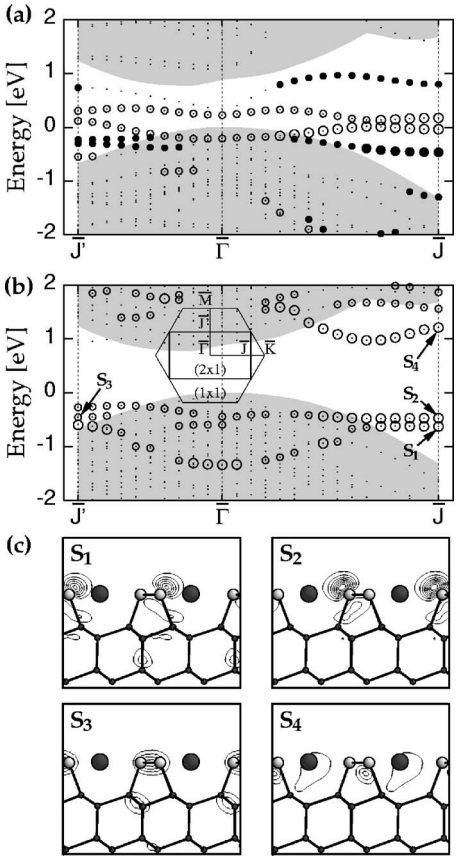

FIG. 3. (a) Surface band structure of the clean Si(111)2×1 surface based on Seiwatz chains: filled (open) circles represent the surface states for the buckled (unbuckled) chain configuration. (b) Surface band structure of the Ca adsorbed Seiwatz-T_4 model. (c) Charge characters of the representative surface states marked in (b). In the contour plot, a uniform increment of 0.02 $e/\text{Å}^3$ is used.

chain. On the clean surface, the unbuckled Seiwatz chain structure has a nearly metallic surface band structure and is subject to a buckling transition as a way of lowering the energy by opening a large band gap.[24] In Ca/Si(111)2×1, however, the partially filled Si dangling-bond states can be saturated by electrons donated from Ca atoms, which eliminates the energy lowering mechanism via buckling and thus recovers the unbuckled chain structure of less strain.

Figure 4 shows simulated STM images of the Seiwatz chain models for Ca/Si(111)2×1. The Seiwatz-T_4 model produces an empty-state image of bright stripes representing the 4*s* states of Ca atoms adsorbed on the T_4 site. The empty-state image of the Seiwatz-H_3 model looks similar, but the bright stripes are uniformly shifted reflecting the different adsorption site. Both models produce almost identical filled-state images of a hexagonal lattice of bright spots corresponding to the dangling-bond states of the Si atoms in the Seiwatz chains. These STM images reflect well the calculated band characters shown in Fig. 3 and are also consistent with the STM features of the AM/Si(111)3×1 surfaces,[4,5] i.e., empty-state images of bright stripes derived from alkali atoms and filled-state images of triangular lobes (here, appearing as an image of double chains) representing the Si dangling bonds of the honeycomb chains. Previous STM measurements for the Ca/Si(111)2×1 surface, however, reported only bright stripes in both empty- and filled-state images.[16,17] Thus, while the empty-state images are in good agreement between experiment and theory, the simulated filled-state image of hexagonal lobes appears different from the experimental image of stripes. In view that our simulated STM images little change with either sampled bias voltage or

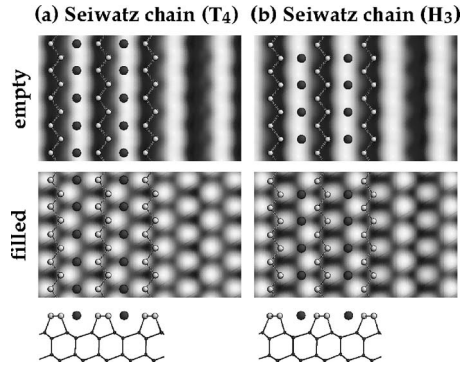

FIG. 4. Simulated constant-current STM images of Ca/Si(111)2×1: (a) Seiwatz chain (T_4) and (b) Seiwatz chain (H_3). The empty-state images were obtained by integrating $\rho(r,E)$ from E_F to $E_F+1.5$ eV and the filled-state images from $E_F-1.5$ eV to E_F. Both images are taken at $\rho=7\times10^{-4}$ $e/\text{Å}^3$.

sampled charge density, the atomic structure of the Si(111)2×1 surface may require further investigation by such as high-resolution STM or x-ray diffraction.

In summary, we have investigated the Ca/Si(111)2×1 surface using density functional theory calculations. The Seiwatz-T_4 model, suggested by experiments, is confirmed to be energetically stable. This model produces a semiconducting band structure with two filled bands derived from the Si dangling bonds of the Seiwatz chain and one empty band from the 4*s* state of Ca. While the calculated surface bands agree well with ARPES data, it remains a problem that the simulation for the Seiwatz-T_4 structure does not reproduce the measured filled-state STM images of 1D stripes.

Note added in proof. Miwa has recently reported a density-functional study of the Ca/Si(111)2×1 surface using local density approximation and linear combinations of atomic orbitals.[29] The surface band structure and STM images reported for the Seiwatz chain (T_4) structure are similar to the present results.

This work was supported by Korea Research Foundation Grant (KRF-2004-C040704) and by POSTECH BSRI research fund-2005. Computations have been performed using supercomputers at POSTECH and at the Korea Institute of Science and Technology Information.

*E-mail address: kang@postech.ac.kr

[1] H. Daimon and S. Ino, Surf. Sci. **164**, 320 (1985).
[2] C. Collazo-Davila, D. Grozea, and L. D. Marks, Phys. Rev. Lett. **80**, 1678 (1998).
[3] L. Lottermoser, E. Landemark, D. M. Smilgies, M. Nielsen, R. Feidenhans'l, G. Falkenberg, R. L. Johnson, M. Gierer, A. P. Seitsonen, H. Kleine, H. Bludau, H. Over, S. K. Kim, and F. Jona, Phys. Rev. Lett. **80**, 3980 (1998).
[4] S. C. Erwin and H. H. Weitering, Phys. Rev. Lett. **81**, 2296 (1998).
[5] M. H. Kang, J. H. Kang, and S. Jeong, Phys. Rev. B **58**, R13359 (1998).
[6] J. Quinn and F. Jona, Surf. Sci. **249**, L307 (1991).
[7] O. Kubo, A. A. Saranin, A. V. Zotov, J. T. Ryu, H. Tani, T. Harada, M. Katayama, V. G. Lifshits, and K. Oura, Surf. Sci. **415**, L971 (1998).
[8] G. Lee, S. Hong, H. Kim, D. Shin, J. Y. Koo, H. I. Lee, and Dae Won Moon, Phys. Rev. Lett. **87**, 056104 (2001).
[9] H. W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schaefer, C. M. Lee, S. D. Kevan, T. Ohta, T. Nagao, and S. Hasegawa, Phys. Rev. Lett. **82**, 4898 (1999).
[10] S. J. Park, H. W. Yeom, S. H. Min, D. H. Park, and I. W. Lyo, Phys. Rev. Lett. **93**, 106402 (2004).
[11] J. H. Cho, J. Y. Lee, and L. Kleinman, Phys. Rev. B **71**, 081310(R) (2005).
[12] L. D. Marks and R. Plass, Phys. Rev. Lett. **75**, 2172 (1995).
[13] M. H. Kang and J. Y. Lee, Surf. Sci. **531**, 1 (2003).
[14] S. C. Erwin, Phys. Rev. Lett. **91**, 206101 (2003).
[15] S. Riikonen and D. Sanchez-Portal, Phys. Rev. B **71**, 235423 (2005).
[16] A. A. Baski, S. C. Erwin, M. S. Turner, K. M. Jones, J. W. Dickinson, and J. A. Carlisle, Surf. Sci. **476**, 22 (2001).
[17] T. Sekiguchi, F. Shimokoshi, T. Nagao, and S. Hasegawa, Surf. Sci. **493**, 148 (2001).
[18] K. Sakamoto, W. Takeyama, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B **66**, 165319 (2002).
[19] D. Y. Petrovykh, K. N. Altmann, J. L. Lin, F. J. Himpsel, and F. M. Leibsle, Surf. Sci. **512**, 269 (2002).
[20] O. Gallus, Th. Pillo, P. Starowicz, and Y. Baer, Europhys. Lett. **60**, 903 (2002).
[21] Y. K. Kim, J. W. Kim, H. S. Lee, Y. J. Kim, and H. W. Yeom, Phys. Rev. B **68**, 245312 (2003).
[22] K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B **69**, 125321 (2004).
[23] K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B **68**, 245316 (2003).
[24] S. H. Lee and M. H. Kang, Phys. Rev. B **54**, 1482 (1996).
[25] B. Chen and D. Haneman, Phys. Rev. B **51**, 4258 (1995).
[26] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).
[27] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).
[28] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[29] R. H. Miwa, Phys. Rev. B **72**, 085325 (2005).