Stability of Sb line structures on Si(001)

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Structure and stability of Sb-dimer linear chains on the Si(001) surface are studied by means of *ab initio* quantum-mechanical molecular dynamics using pseudopotentials. It is confirmed that the model comprising a double core of seven-membered rings of silicon for Bi/Si(001) nanolines is indeed one of the most stable structures energetically, and it also explains Sb/Si nanolines. Moreover, it is clear that stability of the odd-membered-ring (5-7-5) structure will decrease as the group-V adatom changes from Bi to Sb, and disappear for As/Si due to the size effect.

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Group-V elements such as Bi, Sb, and As on Si(001) surfaces are technologically important as surfactants as well as dopants.[1] Upon Bi or Sb adsorption on Si(001), two kinds of reconstructed surface phases, $(2\times n)$ (Refs. 2–4) and $c(4\times 4)$,[5,6] are found to form depending on both the coverage and the substrate temperature. In the case of Bi, for example, one observes a series of $(2\times n)$ phases, with n varying continuously from 5 to 12.[3] Moreover, a more striking phenomenon, namely, Bi-dimer line structure[6–13] is also found on the terraces of Si(001) under a selective adsorption or desorption process around a critical temperature. Techniques to form one-dimensional structures such as this Bi-dimer line may be applicable to the fabrication of atomic scale devices on a semiconductor surface.

The formation of this line structure consisting of Bi dimers was first found and reported by Naitoh *et al.* in 1997.[11] They investigated the bismuth-induced structure on Si(001) surfaces by scanning-tunneling microscopy (STM) and showed that bismuth atoms formed long lines as belts on the Si(001) topmost layer after annealing at around 500 °C. Each belt consists of two chains of bismuth dimers,[13] and the dimerization direction is parallel to the chain and perpendicular to the Si-dimer rows. From the STM images taken after adsorption of hydrogen on the surface,[12,13] they speculated that the linear chains of Bi dimers substitute for four Si-dimer rows on the topmost Si(001) layer. On the other hand, same bismuth lines are also found by Miki *et al.* in 1998.[6–10] They performed detailed studies of both experimental and theoretical works. Although some models of the Bi line structures were proposed earlier,[6,7,14] the correct model comprising a double core of seven-membered rings of silicon was just obtained by Owen *et al.*[10] Recently, line structure similar to the above-mentioned Bi/Si(001) was also found for another group-V element Sb when it is adsorbed on a hydrogen-terminated Si(001) surface.[15] It remains a challenge to understand such line structures from both fundamental and technological viewpoints.

In this paper, to confirm the structural model given by Owen *et al.*[10] for Bi/Si(001), we report a systematic *ab initio* study on the structure and stability of Sb, either adsorbed on or embedded in a Si(001) surface, in a linear-chain form. All calculations are performed by means of first-principles quantum-mechanical molecular dynamics using pseudopotentials and a plane-wave basis set[16,17] under the generalized gradient approximation.[18] Similar simulations for other group-V elements, Bi and As, are also performed for comparison.

In Fig. 1, two models [Figs. 1(b) and 1(d)] consisting of two parallel Sb-dimer chains separated by $\sim 2a$ are shown.[19] Here, $a(=3.84$ Å) is of the ideal lattice constant of Si. In order to understand these Sb linear-chain structures, corresponding structures of clean Si substrates are also shown in Fig. 1(a) and Fig. 1(c). Figures 1(a) and 1(b) represent the bulklike surface with a sixfold ring network; Figs. 1(c) and 1(d) represent a metastable surface involving two odd-membered (5-7-5) rings in sixfold, as given by Owen *et al.*[10] The metastable odd-membered ring structures exist indeed in *a*-Si and *a*-Ge,[20] under a quick cooling process, and are also

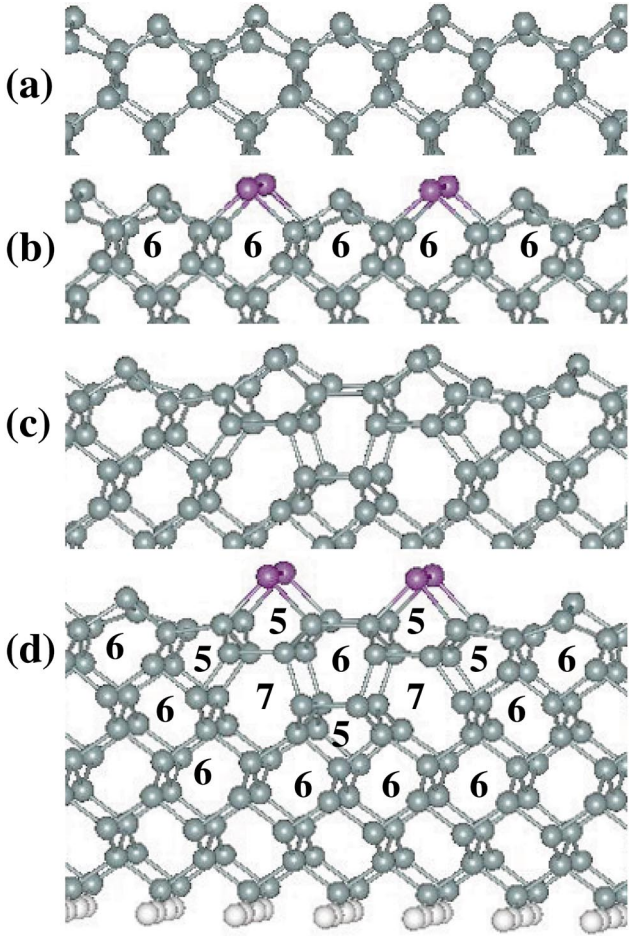

FIG. 1. (Color) Three-dimensional views of linear chains of the Sb dimer on the Si(001) surface after lattice relaxation. (a) and (b) represent a bulklike structure; (c) and (d) are a modified structure involving two odd-membered (5-7-5) rings. Red dots represent Sb, and white dots represent H.

found on the As-terminated Ge(001) surface as reported by Zhang *et al.*[21] To simulate these structures, the supercell size is set to $XYZ = 7.68\ \text{Å} \times 30.72\ \text{Å} \times 35.72\ \text{Å}$ with ten layers of silicon, one layer of hydrogen to passivate the lowest Si layer, and a vacuum layer of about 20 Å in the Z direction. The XY plane corresponds to a 2×8 slab with periodic boundary conditions. For each supercell shown in Fig. 1, the total number of atoms (Si+Sb) are the same. The cross section of the local structure is three dimer rows for Fig. 1(b) and four dimer rows for Fig. 1(d). All structures studied are fully relaxed, so that their structural parameters are obtained at the same time. The electron-ion interaction is described with ultrasoft pseudopotentials.[22] Forces on the ions are calculated through the Hellmann-Feynman theorem allowing a geometry optimization. The minimization of the free energy is done over the atomic and electronic degrees of freedom using the conjugate gradient iterative technique with two k points in the X direction of the Brillouin zone, and 200 eV of the cutoff energy. The convergence is achieved when the maximum force on all atoms is less than 0.01 eV/Å.

The calculated adsorption energies are listed in Table I, for Figs. 1(b) and 1(d), together with (2×8)-Sb and (2×1)-Sb surfaces. Similar calculations are also performed when the adsorbate Sb is replaced by Bi or As. The adsorption energy of the given adatom structure is defined as the energy obtained by the systems with respect to the ideal (2×1)-Si(001) surface plus an isolated Sb (or Bi, As) atom. The calculated structural parameters for Figs. 1(b) and 1(d) are listed in Table II. For all the structures, the dimer bond length, L, is estimated as 3.08, 2.94, and 2.55 Å for Bi-Bi,

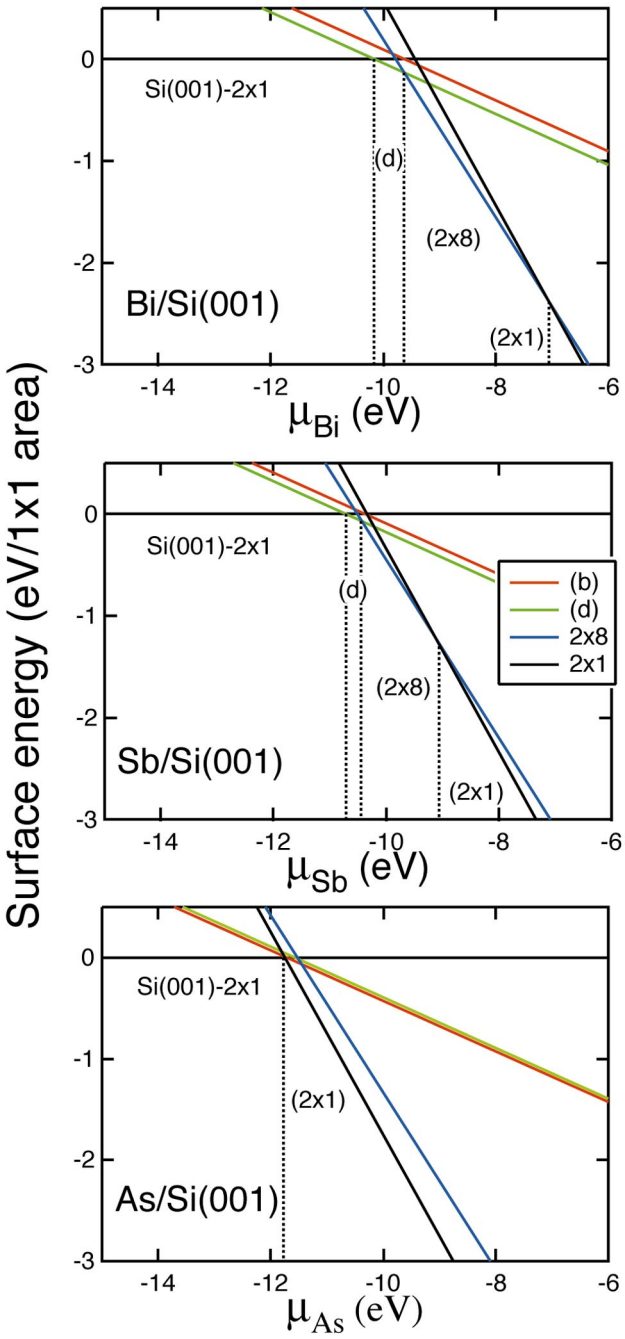

FIG. 2. (Color) Surface energy relative to Si(001)-2×1 clean surface are plotted as a function of the adatomic chemical potential. Left and right sides correspond to the low and high adatomic coverages, respectively. The phase regions are divided by vertical lines. The corresponding bulk chemical potential are -3.896, -4.154 and -4.695 eV per atom for Bi, Sb and As, respectively.

TABLE I. Calculated adsorption energy in eV/dimer for Bi-, Sb-, and As-dimer linear chains on the Si(001) surface with bulklike [Fig. 1(b)] and odd-membered-ring [Fig. 1(d)] structures, respectively. In comparison, the adsorption energy for (2×8) and (2×1) structures of Bi, Sb, and As are also included.

Structure	Bi	Sb	As
Figure 1(b)	−9.80	−10.37	−11.72
Figure 1(d)	−10.16	−10.71	−11.56
(2×8)	−9.78	−10.51	−11.53
(2×1)	−9.44	−10.33	−11.75

Sb-Sb, and As-As, respectively. They are indeed very close to 3.071, 2.906, and 2.507 Å of the nearest-neighbor distances of their bulks. This suggests that the Bi, Sb, and As atoms preserve their properties after adsorption on Si, and the fundamental bonding mechanisms are the same for different group-V elements on the Si(001). However, because of different atomic sizes, their stability varies from system to system. One can expect that compressive stress develops along the dimer row for Fig. 1(b) as Bi embeds in the Si(001) surface,[11,12] while the modified structure of Fig. 1(d) enables such compressive strain energy to be relieved. Thus, Sb/Si(001) as well as Bi/Si(001) favor Fig. 1(d) and As/Si(001) favors the bulklike structure of the Fig. 1(b). The L and also h (height of Sb dimers from the Si topmost layer) decrease as the adatoms change from Bi to As due to the size effect. A similar size effect also appears on the bond angle, θ, of the Si-(Bi,Sb,As)-Si, which increases from Bi to As. On the other hand, the separation distance, d, of the two linear dimer chains stays almost constant, independent of the adatomic element. The calculated d for Sb (or Bi) with Fig. 1(d) is 6.37, which is consistent with 6.28 ± 0.3 of the experimental results.[9] According to these results, we can see that the local structure (L, h, θ) of the adatom is essentially governed by the adatomic properties (size), but the separation d is almost governed by the substrate structures of Si.

It is noted that the most stable structure is the odd-membered-ring structure [Fig. 1(d)] for Sb/Si(001) and Bi/Si(001), although the bulklike structure [Fig. 1(b)] is favored over Fig. 1(d) with −0.15 eV/dimer for As/Si(001); Fig. 1(a) of the Si(001)-2×1 surface is more stable than Fig. 1(c) with the odd-membered-ring by −0.11 eV/dimer. Therefore, the observed Sb (or Bi) linear chain with an odd-membered-ring structure [Fig. 1(d)] must be stabilized by the presence of Sb (or Bi). Such a behavior can also be understood from the different reactions between group-V elements and Si. For the As-Si system, two compounds, AsSi and As_2Si, exist naturally in the equilibrium phase diagram. No counterpart exists for Sb-Si and Bi-Si cases.[23] In Fig. 2, to obtain a systematic understanding of the stability of these phases, the relative surface energy ($E_s - n_{Sb}\mu_{Sb}$) as a function of the chemical potential is shown. Here, the substrate chemical potential is already included in the definition of E_s as taken from Table I, and n_{Sb} is the adatomic coverage. It is found that as the chemical potential of Sb increases (from left to right) the phase will move from a (2×1)-Si clean surface to an odd-membered-ring structure [Fig. 1(d)], to (2×8)-Sb and finally to (2×1)-Sb at high Sb coverage. Similar behavior also exists for the Bi/Si system as shown in Fig. 2(a). However, the region of the structure in Fig. 1(d) for Sb/Si is remarkably narrower compared to that for Bi/Si. Due to the different reactions between group-V elements and the Si(001) surface, Fig. 1(d) does not exist for As/Si.

TABLE II. Calculated lattice parameters, bond length (L), height (h), and bond angle (θ) of Si-(Bi,Sb,As)-Si, and the separation (d) of (Bi, Sb, As) linear dimer chains, for structures in Figs. 1(b) and 1(d).

Structure type	Lattice parameter	Bi	Sb	As
Figure 1(b)	L (Å)	3.08	2.94	2.55
	h (Å)	0.74	0.58	0.44
	θ (°)	93.07	95.65	100.65
	d (Å)	7.81	7.80	7.75
Figure 1(d)	L (Å)	3.08	2.94	2.56
	h (Å)	1.38	1.28	1.04
	θ (°)	85.22	87.39	90.95
	d (Å)	6.38	6.37	6.26

In summary, we have examined the structure and stabilities of the Sb line structure on Si(001) surfaces. It is clear that the linear chains of Sb dimers crossing four Si-dimer rows on the terrace with an odd-membered-ring (5-7-5) structure is one of the most stable structures at low coverage as well as that for Bi/Si(001). However, the stability of the odd-membered-ring (5-7-5) structure will decrease as the adatom changes from Bi to Sb, and disappear for As/Si due to the different reactions between the group-V elements and the Si(001) surface. Throughout this work, we understand that the atomic size plays a major role in stabilizing the line structures. It is understood that during the adsorption or desorption process around the critical temperature not only do Bi atoms desorb, but also Si and H atoms migrate on the surface.[11] The migration mechanism of the formation after atomic hydrogen exposure of the line structure is under further study by our group.

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[1] K. Sakamoto, K. Kyoya, K. Miki, H. Matsuhata, and T. Sakamoto, Jpn. J. Appl. Phys., Part 2 **32**, L204 (1993).
[2] T. Hanada and M. Kawai, Surf. Sci. **242**, 137 (1991).
[3] Ch. Park, R.Z. Bakhtizin, T. Hashizume, and T. Sakurai, Jpn. J. Appl. Phys., Part 2 **32**, L528 (1993).
[4] P. De Padova, R. Larciprete, C. Quaresima, C. Ottaviani, B. Ressel, and P. Perfetti, Phys. Rev. Lett. **81**, 2320 (1998).
[5] A.A. Saranin, A.V. Zotov, V.G. Kotlyar, V.G. Lifshits, O. Kubo, T. Harada, T. Kobayashi, N. Yamaoka, M. Katayama, and K. Oura, Jpn. J. Appl. Phys., Part 1 **40**, 6069 (2001).
[6] K. Miki, J.H.G. Owen, D.R. Bowler, G.A.D. Briggs, and K. Sakamoto, Surf. Sci. **421**, 397 (1999).
[7] K. Miki, D.R. Bowler, J.H.G. Owen, and K. Sakamoto, Phys. Rev. B **59**, 14868 (1999).
[8] M. Shimomura, K. Miki, T. Abukawa, and S. Kono, Surf. Sci. **447**, L169 (2000).
[9] J.H.G. Owen, D.R. Bowler, and K. Miki, Surf. Sci. **499**, L124 (2002).
[10] J.H.G. Owen, K. Miki, H. Koh, H.W. Yeom, and D.R. Bowler, Phys. Rev. Lett. **88**, 226104 (2002).
[11] M. Naitoh, H. Shimaya, S. Nishigaki, N. Oishi, and F. Shoji, Surf. Sci. **377**, 899 (1997).
[12] M. Naitoh, M. Takei, S. Nishigaki, N. Oishi, and F. Shoji, Jpn. J. Appl. Phys., Part 1 **39**, 2793 (2000).
[13] M. Naitoh, M. Takei, S. Nishigaki, N. Oishi, and F. Shoji, Surf. Sci. **482-485**, 1440 (2001).
[14] D.R. Bowler, Phys. Rev. B **62**, 7237 (2000).
[15] O. Kubo, J.T. Ryu, H. Tani, T. Harada, T. Kobayashi, M. Katayama, and K. Oura, Appl. Surf. Sci. **169-170**, 93 (2001).
[16] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[17] G. Kresse and J. Furthmuller, Comput. Mater. Sci. **6**, 15 (1996).
[18] J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademic-Verlag, Berlin, 1991), p. 11.
[19] In the present work, the typical adatomic structure on the Si(001) surface with a fourfold ring network, and the structure involving the substitution of the two Bi dimers for two Si dimers with a missing dimer defect shown in Fig. 3(a) in K. Miki, D.R. Bowler, J.H.G. Owen, and K. Sakamoto, Phys. Rev. B **59**, 14868 (1999) are also studied. They are all unstable energetically, and thus are neglected.
[20] R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).
[21] S.B. Zhang, W.E. McMahon, J.M. Olson, and S.-H. Wei, Phys. Rev. Lett. **87**, 166104 (2001).
[22] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[23] T. B. Massalski, J. L. Murray, L. H. Bennet, and H. Baker, *Binary Alloy Diagrams* (American Society for Metals, Metals Park, OH, 1986).