Stress relief from reconstructions on Sb/Si(001)

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The structures and stress of the Sb/Si(001) surface have been studied by a semiempirical tight-binding Green's function method. The Sb/Si(001)2×1 surface is found to be under a tensile stress of 1.0 eV/(1×1 cell) along the dimer bond and a compressive stress of -1.1 eV/(1×1 cell) along the dimer row. Calculations of the surface stress for Sb/Si(001) (2×4), (2×5), and (2×6) reconstruction, which is formed by shifting dimers in the dimer row to the adjacent trench, show a significant relief of the compressive contribution to the stress along the dimer row comparing with the case of the (2×1) reconstruction, and thus a decrease of the stress anisotropy.

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It is well known that As or Sb as a surfactant will mediate the epitaxial growth of Ge on Si surfaces and form symmetric dimers on the (2×1) reconstruction on Si(001) surface.[1–6] However, scanning tunneling microscopy (STM) images[1] show that Sb/Si(001) surface is considerable less ordered than As/Si(001) surface and the long-range (2×1) order is broken up by a high density of defects–either voids or antiphase domain boundaries (APB's) on Sb/Si(001), and the symmetric Sb dimers are not arranged in the long ordered (2×1) reconstruction. Although Sb and As belong to the same group, in contrast to the Sb case, the APB's were rarely observed on the As/Si(001) surface, which exhibits a perfect (2×1) reconstruction.[1,7,8] Interestingly, the Sb/Si(001) surface has been shown to take on a ($2\times n$) surface reconstruction in low-energy electron diffraction (LEED) pattern.[9]

Gonzalez Mendez and Takeuchi[10] studied the difference between the adsorption of As and Sb on Si(001) surface. They concluded that kinetic effects play a crucial role dictating whether the surface is completely ordered or it contains antiphase domain boundaries. Due to the general consensus that surface stress plays an important role in some surface reconstructions, it has been suggested that appearance of the defects on the Sb/Si(001) surface can be explained by stress relief.[7,8,11,12] However, to our knowledge, neither theoretical nor experimental work has determined the stress and its change in this case quantitatively.

In order to understand the experimental observations of Sb and As on Si(001) surface, we report calculation results of the change in surface stress of these reconstruction surfaces, which are formed by shifting one or two dimers of the (2×1) reconstruction to the trench between two dimer rows. We will study the structure and stress of Sb/Si(001) surface to uncover the essential physical mechanism involved in the phenomena. We will interpret the origin of the high density of defects on the Sb/Si(001) surface and give direct information about the actual amount of stress relieved in Sb/Si(001) reconstructions. We should conclude that the driving force of defects of the (2×1) reconstructions could be contributed primarily to the large stress anisotropy.

We adopt a semiempirical approach for calculating the surface stress, which was proposed in our previous work.[13,14] In this approach, the surfaces are treated as a semi-infinite slab. This approach is based on Chadi's total energy model[15] and the tight-binding Green function method.[16] A strained system is treated as a perturbation of an unstrained system and the corresponding stresses are calculated by the Green function method.[13]

The interaction parameters up to the second-nearest neighbors of Si and Sb as well as that between Si and Sb were determined by fitting its band structures to our own *ab initio* calculation results. The SiSb and Sb pseudocrystals have zinc blende structure and diamond structure, respectively. Their lattice constants were obtained by the minimization of total energy. The *ab initio* calculations were performed by the *ab initio* molecular dynamics package of the Car-Parrinello-like scheme[17] FHI96MD (Ref. 18) based on the framework of local density functional theory (LDFT). The Ceperley and Alder exchange-correlation form[19] parameterized by Perdew and Zunger[20] and the fully separable *ab initio* pseudopotentials[21] for Si and Sb were used. We used plane waves with a kinetic energy up to 22.0, 25.0, and 25.0 Ryd for Si, Sb, and SiSb, respectively. The **k** points are sampled on a uniform grid of not less than 64 points.

We will first focus on the completely ordered Sb/Si(001) (2×1) surface. A schematic top view of the Sb/Si(001) (2×1) surface is given in Fig. 1(a). Based on the 2×1 geometry, the equilibrium structure of one monolayer of Sb on a Si(001) semi-infinite substrate is determined. Only the relaxation of the top six surface layers is taken into account, because relaxation in deeper layers has no numerically significant effect on structure and stress.[13] The optimizing procedure to determine the structure of Sb on the Si(001) surface has been described in Refs. 22,23.

As shown in Table I, the displacements of Si atoms from bulk positions are all within 0.10 Å. The length of the Sb-Sb dimer bond is found to be $d_D=2.93$ Å, and the backbond length between Sb and the subsurface Si atom is found to be $d_{12}=2.59$ Å, comparing well with the results of SEXAFS and STM experiments[1] $d_D=2.88$ Å and $d_{12}=2.63$ Å, as well as the values of LDA calculations of Tang *et al.*[3] $d_D=2.93$ Å and $d_{12}=2.61$ Å, and of Cho *et al.*[2] $d_D=2.94$ Å and $d_{12}=2.59$ Å. The present results further confirm previous theoretical and experimental results that the Si substrate shows a bulklike structure after Sb adsorption.[1–6]

When compared the adsorption of As and Sb on Si(001), we found some differences in the surface structures. These

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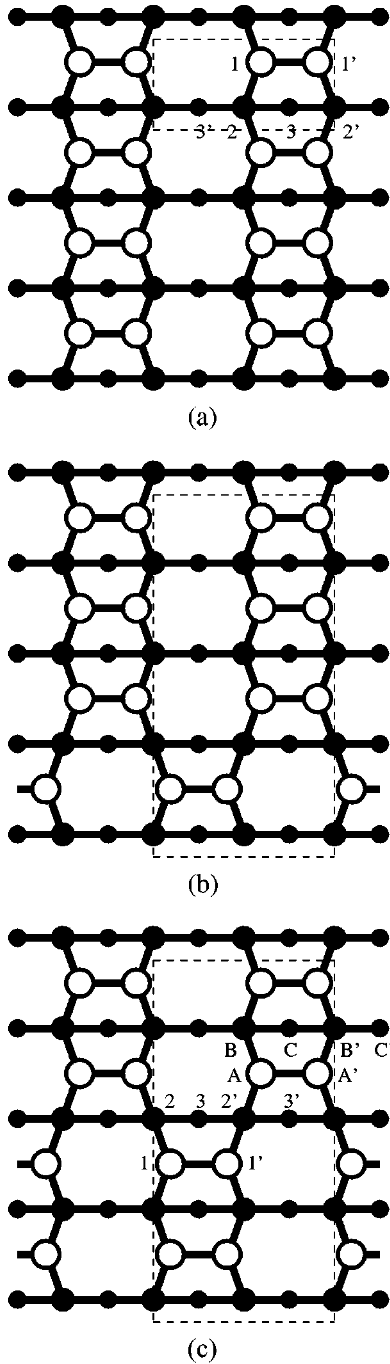

FIG. 1. Top view of (a) Sb/Si(001)(2×1), (b) Sb/Si(001)(2×4)-A, and (c) Sb/Si(001)(2×4)-B models with Si atoms shaded.

differences can be related to the different covalent radii of As and Sb. The covalent radii of Sb is about 14% larger than that of As. For As on Si(001), the length of As-As dimer bond is 2.47 Å,[13] while for Sb on Si(001) the length of Sb-Sb dimer bond is 2.93 Å. Thus the As atom pulls the Si atoms below it to close to As dimer by 0.19 Å, and pushes the sublayer Si atoms near the center of As dimer downwards by 0.18 Å, and elevates the sublayer Si atoms away from the center of As dimer upwards by 0.17 Å. In contrast, the Si atoms are in their bulklike positions after Sb adsorption, as shown in Table I and Ref. 13. It is worth noting that the length of Sb-Sb dimer bond for Sb/Ge(001) is 2.95 Å.[26]

TABLE I. The atomic displacements relative to the corresponding position of an ideal Si for Sb on Si(001)2×1 surface, in Å. x and z represent the direction parallel to the dimer bond and the direction perpendicular to the surface, respectively. The atom notations please refer to Fig. 1(a).

Layer	Δx	Δz	$\Delta x'$	$\Delta z'$
1	0.44	0.36	-0.44	0.36
2	0.08	0.01	-0.08	0.01
3	0.00	0.06	0.00	-0.10

After we determined the optimal geometry, the surface stress of Sb/Si(001)2×1 was calculated using the aforementioned method. The stress along the dimer bond is found to be tensile $\sigma_{\parallel}=1.0$ eV/$(1\times1$ cell), while the stress along the dimer row is compressive $\sigma_{\perp}=-1.1$ eV/$(1\times1$ cell). The anisotropy of surface stress is thus $F=\sigma_{\parallel}-\sigma_{\perp}=2.1$ eV/$(1\times1$ cell), compared with the results of As/Si(001)2×1, $\sigma_{\parallel}=2.1$ eV/$(1\times1$ cell), $\sigma_{\perp}=2.0$ eV/$(1\times1$ cell), and $F=0.1$ eV/$(1\times1$ cell).[13] Obviously, there are notable differences between the adsorption of As and Sb on Si(001) substrate. In contrast to the case of As adsorption on Si(001), the stress of Sb on Si(001) along the dimer row is compressive rather tensile, and the anisotropy of surface stress is thus much larger than that of As on Si(001).

It was found by experiments that there is a high density of defects on Sb/Si(001) surface, namely, antiphase domain boundaries (APB's).[8] In order to understand the effect of these phenomena on Sb/Si(001) surface, we simulate the APB's, which form perpendicular to the dimer rows, by (2×4), (2×5), and (2×6) reconstruction. A top view of the (2×4) reconstruction is shown in Figs. 1(b) and 1(c), here two boundaries are separated by one and two dimers, respectively. Although the observed $(2\times n)$ reconstruction[9] had an n of 11, our models have contained two essential features of the $(2\times n)$ domain: there is enough space to break interactions between boundaries because only interactions of second nearest neighbor are taken into account in our tight-binding model; there is no symmetric restriction in the direction of dimer row comparing with the (2×1) reconstruction because one part of a dimer row has been shift to the nearest trench.

The (2×4)-A model is obtained by shifting one dimer of each row of the completely ordered Sb/Si(001) (2×1) to the nearest trench, and the (2×4)-B one by shifting two dimers of each row, as shown in Figs. 1(b) and 1(c), respectively. The white circles in the figure represent Sb atoms, and the big and small black circles represent Si atoms of the first and second layer, respectively. The (2×5) model is obtained by shifting two dimers, while the (2×6) one by shifting three dimers to the nearest trench.

We found that the (2×4), (2×5), and (2×6) reconstruction of Sb/Si(001) have similar structures and stress. Thus, we focus on the Sb/Si(001) (2×4) surface below. Repeating the same calculation procedure, the optimal structures for Sb/Si(001) (2×4)-A and (2×4)-B reconstructions have been obtained. Comparing with the ordered Sb/Si(001)

TABLE II. The same as Table I, but for Sb/Si(001)2×4-*B*. *y* represents the direction perpendicular to the dimer bond. The atom notations please refer to Fig. 1(c).

Atom	Δ_x	Δ_y	Δ_z	Atom	Δ_x	Δ_y	Δ_z
1	0.44	0.01	0.36	A	0.44	−0.01	0.36
1′	−0.44	0.01	0.36	A′	−0.44	−0.01	0.36
2	0.00	0.00	0.02	B	0.07	0.00	0.02
2′	0.00	0.00	0.02	B′	−0.07	0.00	0.02
3	0.00	0.06	−0.01	C	0.00	0.00	−0.08
3′	0.00	−0.06	−0.01	C′	0.00	0.00	0.06

(2×1), we found that the structures of the both (2×4) reconstructions are similar to that of Sb/Si(001) (2×1). The obvious difference is in the relaxation in the direction perpendicular to the dimer bond. Since there is no restriction of symmetry in this direction, we found a 0.01 Å relaxation of the Sb layer in the direction of perpendicular to the dimer bond for the both (2×4)-*A* and -*B* reconstruction. The structural parameters of the Sb/Si(001) (2×4)-*B* are listed in Table II. We can see from the table that the relaxation in the direction perpendicular to the dimer bond is very small. Calculations for the both reconstructions also show that the substrate Si atoms are kept in a bulklike configuration after Sb adsorption, and the displacements of Si atoms from the bulk positions are all within 0.08 Å, as in the case of Sb/Si(001)2×1. However, there are also some relaxations along the dimer row for both the Sb and Si atoms. So the bonding between Sb and substrate Si can extend in the direction perpendicular to the dimer bond, and reduce the relaxation in the direction perpendicular to the surface.

We calculate the stress for the optimal structures for the both Sb/Si(001) (2×4) reconstructions. For both models, the stress along the dimer bond is tensile, $\sigma_{\parallel}=1.0$ eV/$(1\times1$ cell), and nearly equal to that of the (2×1) reconstruction, but the stress along the dimer row decreases about 27%, $\sigma_{\perp}=-0.8$ eV/$(1\times1$ cell), and the stress anisotropy is $F=\sigma_{\parallel}-\sigma_{\perp}=1.8$ eV/$(1\times1$ cell), while the stress and stress anisotropy for As/Si(001) (2×1) and (2×4) are almost unchanged. Since there is no symmetry restriction along the dimer row, the Sb atoms can relax in this direction to relieve the stress. Although the relaxation along the dimer row is small, it is a significant factor in relieving the compressive contribution to the stress. Since the stress along the dimer bond stems from the fact that the atoms in the dimers would like to be closer together, the stress $\sigma_{\parallel}$ along the dimer bond is tensile and is almost unchanged (the dimer bond length is almost unchanged with the atom's relaxation). For the Sb/Si(001) (2×1) reconstruction, the Sb atom in dimer pushes the Si atoms under it outwardly in the direction of the dimer row, and vice versa. This effect tends to make the Sb as well as the Si atomic distance in this direction longer. Because the symmetry prevents the relaxation of atoms along the dimer row, the surface is subjected to compressive stress. From a simple point of view the dimers are more compressed in this direction due to the larger atomic size of Sb atom. In addition to atomic size and chemical effects, surface stress may also result from any unusual bonding configurations present at a surface.[24] We thus infer that the Sb/Si(001) (2×1) surface is subjected to compressive stress. This effect will break the restriction by shifting the dimers to the nearest trench between dimer rows in order to relieve the stress as much as possible. Once the Sb atoms can relax along the dimer row by shifting dimers, the dimers will be less close-packed along dimer row and the compressive stress will be relieved significantly. Thus the stress along the dimer row decreases. With the dimers jammed to the adjacent trenches during the growth, the stress is relieved, the APB's start to form, and the Sb/Si(001) surface gradually becomes more stable and indicates imperfect 2×1 reconstruction.

The stress anisotropy $F=\sigma_{\parallel}-\sigma_{\perp}$, which may cause an instability in the surface morphology,[25] decreases significantly for the both (2×4) reconstructions because of the significant relief of the compressive contribution to the stress along the dimer row, when compared with the completely ordered (2×1) surface. Alerhand *et al.* demonstrated that the spontaneous formation of stress domains is a natural consequence of the anisotropy in the intrinsic surface stress caused by the dimerization.[25] The APB can also be seen as a kind of domain wall, across which a dimer string is converted to a trench or vice versa. Accordingly, there is a microscopic stress anisotropy, which can be related to the different structure and strain from the end of a dimer string to the end of a trench. However, both parallel and perpendicular components of the surface stress on As/Si(001) are tensile and the As-As dimer can hardly be shifted to the adjacent trenches.[10] In the case of As/Si(001), there is only a small stress anisotropy, $F=0.1$ eV/$(1\times1$ cell), and the formation of APB is unfavorable.

We calculate the planar stresses parallel and perpendicular to the dimer bond for the Sb/Si(001) (2×1) and (2×4)-*B* reconstruction. For both reconstructions, the sum of the planar stress parallel and perpendicular to the dimer bond approaches constant values with the atomic layers up to the four surface layers, which means that the contribution to the planar stress from Si atomic layers below the top three layers are almost zero. For the Sb/Si(001) (2×1), the planar stress of the top three layers parallel to the dimer bond is 0.50, 0.20, and 0.22 eV/$(1\times1$ cell), respectively, while that perpendicular to the dimer bond is -0.60, -0.59, 0.02 eV/$(1\times1$ cell). Comparing with the Sb/Si(001) (2×1), the planar stress parallel to the dimer bond for the Sb/Si(001) (2×4) is almost unchanged, and the change in surface stress perpendicular to the dimer bond is mainly contributed by the topmost two layers, namely, -0.53 and -0.35 eV/$(1\times1$ cell) for the Sb layer and the first layer of Si substrate, respectively. This also accounts for the atomic relaxations since there is no symmetry restriction in this direction.[27]

Similar features have been obtained for the Sb/Si(001) (2×5) and (2×6) reconstruction, namely, the both are also under a tensile stress of 1.0 eV/$(1\times1$ cell) along the dimer bond and compressive stress of -0.8 eV/$(1\times1$ cell) along the dimer row. In summary, we have studied the structure and surface stress of Sb/Si(001). Calculated results show that the Sb/Si(001) (2×1) surface is under tensile stress of 1.0 eV/$(1\times11$ cell) along the dimer bond and compressive stress of -1.1 eV/$(1\times1$ cell) along the dimer row, the stress

anisotropy is 2.1 eV/(1×1 cell), and the main contribution of surface stress stems from the top three layers. The stress anisotropy of Sb/Si(001) with the defects decreased greatly, from 2.1 eV/(1×1 cell) for the completely ordered (2×1) to 1.8 eV/(1×1 cell) for the (2×4), (2×5), and (2×6) reconstruction. But the stress anisotropy of As/Si(001)2×1 is 0.1 eV/(1×1 cell), and it is almost unchanged for As/Si(001) (2×4). The defects of (2×1) reconstructions on Sb/Si(001) are mainly induced by the significant relief of the compressive contribution to the stress in the direction along the dimer row and thus by the decrease of the stress anisotropy. Thus, we identify the large anisotropy of surface stress as the *primary* driving force of defects and APBs on the Sb/Si(001) surface.

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[1] M. Richter, J.C. Woicik, J. Nogami, P. Pianetta, K.E. Miyano, A.A. Baski, T. Kendelewicz, C.E. Bou-ldin, W.E. Spicer, C.F. Quate, and I. Lindau, Phys. Rev. Lett. **65**, 3417 (1990).

[2] Jun-Hyung Cho, Myung-Ho Kang, and Kiyoyuki Terakura, Phys. Rev. B **55**, 15 464 (1997).

[3] S. Tang and A.J. Freeman, Phys. Rev. B **47**, 1460 (1993).

[4] B.D. Yu and A. Oshiyama, Phys. Rev. B **50**, 8942 (1994).

[5] P.F. Lyman, Y. Qian, and M.J. Bedzyk, Surf. Sci. **325**, L385 (1995).

[6] S.J. Jenkins and G.P. Srivastava, Phys. Rev. B **56**, 9221 (1997).

[7] J. Nogami, A.A. Baski, and C.F. Quate, Appl. Phys. Lett. **58**, 475 (1991).

[8] B. Garni, I.I. Kravchenko, and C.T. Salling, Surf. Sci. **423**, 43 (1999).

[9] J. Falta, D. Bahr, A. Hille, G. Materlik, M. Kammler, and M. Horn-von Hoegen, Appl. Phys. Lett. **69**, 2906 (1996).

[10] M.E. González Méndez and Noboru Takeuchi, Surf. Sci. **432**, 239 (1999).

[11] Richard J. Needs, Phys. Rev. Lett. **58**, 53 (1987).

[12] Dieter Wolf, Phys. Rev. Lett. **70**, 627 (1993).

[13] J.G. Che, K.M. Zhang, and X.D. Xie, Phys. Rev. B **60**, 4784 (1999).

[14] Y. He and J.G. Che, Acta Phys. Sin. **49**, 1747 (2000).

[15] D.J. Chadi, Phys. Rev. Lett. **41**, 1062 (1978).

[16] J. Pollmann, In *Festkörperprobleme (Advances in Solid State Physics)* (Vieweg, Braunschweig, 1980), Vol. 20, p. 117; A. Mazur and J. Pollmann, Phys. Rev. B **39**, 5261 (1989).

[17] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[18] M. Bockstedte, A. Kley, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).

[19] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[20] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[21] X. Gonze, P. Käckell, and M. Scheffler, Phys. Rev. B **41**, 12 264 (1990); X. Gonze, R. Stumpf, and M. Scheffler, *ibid.* **44**, 8503 (1991); M. Fuchs and M. Scheffler, Comput. Phys. Commun. (to be published).

[22] J.G. Che, K.M. Zhang, and X.D. Xie, Phys. Rev. B **50**, 18 167 (1994).

[23] J.G. Che, A. Mazur, and J. Pollmann, Phys. Rev. B **51**, 14 470 (1995).

[24] R.D. Meade and D. Vanderbilt, Phys. Rev. Lett. **63**, 1404 (1989).

[25] O.L. Alerhand, D. Vanderbilt, R.D. Meade, and J.D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).

[26] N. Takeuchi, Phys. Rev. B **55**, 2417 (1997).

[27] We note that significant displacements of subsurface atoms on clean Si surface could raise the energy of APB's much. Therefore, the only way to relax the surface stress on the clean Si (001) surface is the formation of monatomic steps, not the formation of APB's, such boundaries exist on the clean surface only as a metastable feature caused by homoepitaxial growth in the nucleation regime. Please refer to, e.g., the paper by R.J. Hamers, U.K. Koehler, and J.E. Demuth, J. Vac. Sci. Technol. A **8**, 214 (1990).