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The reconstruction of the Si(110) surface and its interaction with Si adatoms

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The reconstruction of the Si(110) surface and the chemisorption of the Si atom on this surface are investigated using a tight-binding molecular-dynamics scheme incorporating Green's-function methods. The present method belongs to a more general class of the embedding methods that have the advantage of allowing an efficient embedding of a finite subspace in an infinite or semi-infinite substrate. Our results support the rotational model for surface reconstruction of the $n\times1(n\geqslant1)$ type. The reconstruction of the Si(110) surface was found to be removed, in general, upon chemisorption with Si adatoms and selectively in the presence of surface vacancies. [S0163-1829(97)05228-4]

The unreconstructed Si(110) surface consists of parallel zigzag chains, widely separated by deep valleys. Until recently, the reconstruction of this surface had not been clarified with any certainty. Earlier [1,2] and recent experimental works[3–6] suggest various reconstructions for Si(110), that include the 2×1, 5×1, 7×1, 9×1, 4×5, 5×4, 16×2, and 32×2 phases whose appearance depends, in most cases, on the temperature and on the Ni contamination of this surface.[3–6] Studies of Ni contaminated surfaces[3,4,6] suggest impurity contamination of the surface to play a dominant role in the surface reconstruction. Ni atoms, for instance, have been found to induce many of the reconstructions of the Si(110) surface, although they were not included directly into the unit cell of these reconstructed surfaces.[3,6] The interpretation of the observed reconstructions has been the subject of various model descriptions. They include the following: (i) the surface rumpling model,[3] proposed for the interpretation of the 16×2 phase; (ii) the adatom-dimer model,[6] proposed for the explanation of most the reconstruction phases, and (iii) the rotational model,[7,8] suggested for the description of a 1×1 phase, which, however, has not been observed experimentally. According to the rotational model, the 1×1 and, as will be shown in the present work, the $n\times1$ reconstructions with $n\geqslant2$, n being an integer, may be described by alternate inward-outward displacements of atoms that result in a rotation (accompanied by a small displacement) of each chain of the (110) surface.

The description of the Si(110) surface relaxation properly is an important first step in the study of its interaction with various adatoms and adclusters. Of particular interest is the study of interactions between Si adatoms with the Si surfaces, providing a crucial first step in the understanding of the fundamental growth mechanism of Si on Si substrates.[9–11] In the present work we make use of the tight-binding molecular-dynamics (TBMD) scheme, incorporating real-space Green's-function methods,[12] to investigate the reconstruction of the Si (110) surface and its interaction with Si adatoms.

The Green's-function approach is ideally suited for the treatment of infinite systems with reduced symmetry (such as surfaces and isolated defects). The technique consists of replacing the original infinite Hamiltonian by a relatively small effective Hamiltonian, called the subspace Hamiltonian (SH),[12] embedded in a frozen semi-infinite crystal, called the substrate. The atoms belonging to the subspace are allowed to move; they are treated using the same TBMD approach as used for the free clusters.[13,14] The subspace Hamiltonian contains the Hamiltonian for the free cluster and an additional term describing the interaction of the subspace with the rest of the semi-infinite crystal. The embedding Hamiltonian is obtained from the Green's function of the ''unperturbed'' substrate. As a result, the SH becomes energy dependent. Essentially, the SH method is the tight-binding analogue of the embedding method of Inglesfield,[15] as shown by Baraff and Schluter.[16] The SH method has been successfully employed in describing the interactions of semiconductor and metal atoms with semiconductor surfaces,[12] as well as the excited states of embedded atoms in jellium.[17]

The size of the subspace is determined by the range of the defect potential rather than the range of defect wave functions as in the supercell case. In the present applications the short-ranged nature of the defect potential allows use of relatively small subspaces for obtaining reasonably accurate results. In order to simulate the reconstruction of the Si(110) surface, we choose a 28-atom subspace embedded in a semi-infinite substrate. Twelve of these atoms belong to the sur-

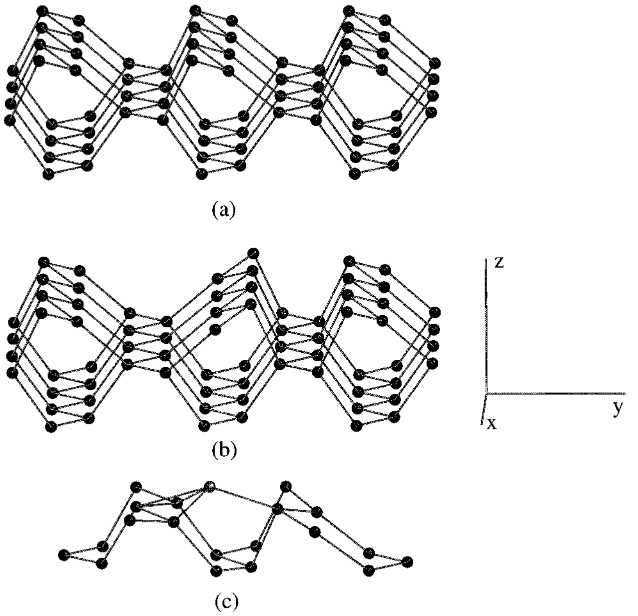

FIG. 1. The (a) 1×1 and (b) 2×1 reconstructions of the Si(110) surface showing the first three substrate layers. Most of the relaxation is confined to the first two layers. The alternate Si surface atoms move outward and inward, respectively, in the direction perpendicular to the surface. (c) The most stable chemisorption site for a Si adatom on the 1×1 reconstructed surface. As seen in the figure, the Si atom forms four bonds with the substrate atoms.

face layer and twelve belong to the subsurface layer. The remaining four atoms are from the third layer. The subspace is constructed in such a way that two surface atoms per zigzag chain are allowed to move along with all their first neighbors on the surface and subsurface layers. No symmetry constraint is imposed on the atoms that are free to move. Using a combination of annealing and molecular-dynamics relaxation, we find two isoenergetic configurations for surface relaxation. Both indicate a rotation of the surface zigzag chains either in phase or in antiphase, thus giving rise to the 1×1 and 2×1 reconstructions for the Si(110) surface. In our calculations we use the universal tight-binding parameters of Harrison,[7] which give a good band structure for the bulk diamond phase of Si. The parameters, however, are taken to have an exponential distance dependence. The remaining parameter, describing the pairwise repulsion term, is obtained by fitting to the experimental lattice spacing (5.43 Å) for the bulk diamond structure.[12–14] When applied to the Si_2 dimmer, these parameters gave a bond length of 2.28 Å, in very good agreement with the experimental bond length of 2.24 Å, ensuring transferability. Furthermore, the present model also has been used to obtain low-energy structures for small Si clusters,[18] in good agreement with *ab initio* results.[19,20]

In the 1×1 rotational relaxation, we find that each zigzag surface chain is rotated by an angle of $\phi = 27.6°$ about an axis in the surface plane along with Δy and Δz translations of the center of mass of each zigzag chain. The Δy translation moves the chain 0.35 Å along the surface plane and perpendicular to the axis of rotation [Fig. 1(a)], while the Δz displacement moves it 0.13 Å along the z axis (perpendicular to the surface) into the interior of the crystal. The alternate Si atoms move outward and inward, respectively, in the direction perpendicular to the surface. The atoms that move inward reduce the orbital hybridization from sp^3 to sp^2 (more planar). The glide plane symmetry of the unreconstructed surface is removed by this type of reconstruction. The relaxed configuration is similar to the one proposed in Ref. 7 and 8 and our values for ϕ, Δy, and Δz are in very good agreement with those reported by Chadi.[8] In the 2×1 rotational relaxation, the relaxation of individual zigzag chains is identical to the 1×1 relaxation, but each chain is rotated and translated in the direction opposite its neighboring chain [Fig. 1(b)]. Consequently, valleys between the chains are broadened and narrowed alternately. The glide plane symmetry is preserved, but the translational symmetry is reduced to 2×1. The initial Si-Si bond length of 2.35 Å for all nearest neighbors now gives way to bond alternations of 2.35 and 2.40 Å along the zigzag chain on relaxation for both types of reconstructions. We find the 2×1 reconstruction to be almost isoenergetic with the 1×1 reconstruction. No surface dimer formation is obtained for either the 2×1 or the 1×1 reconstruction and therefore our results do not support the dimer model proposed[6] to explain the Si(110) structural phase transitions.

The choice of our subspace, however, does not allow us to exclude the $n\times1$ relaxed configurations, ($n>2$, n being an integer) as possible relaxational phases of the Si(110) surface, all of them attributable to the rotational mechanism. Some of these configurations require the use of larger subspaces. It is of interest to find out if the presence of an adatom (i.e., a Ni atom) or of a vacancy can cause any alteration of the rotation of the surface zigzag chain or change its phase of rotation. We have examined the effects of a vacancy in a surface chain and find that when a vacancy is created in the atoms that move outward, the nearest-neighbor atoms on the same chain that had initially moved inward upon relaxation now move outwards with their z coordinates reaching the same value as those of the atoms that had moved outward. This can be attributed to the tendency of the vacancy to induce a local change in the phase of rotation of the chain. No such effect was found when a vacancy is created in the surface atoms that moved inward on relaxation. These results can be easily understood by observing the charge state of the surface atoms [found by calculating the projected electron density of states (DOS)], which shows that surface atoms that move outward during reconstruction exhibit occupied s valence states, while the atoms that move inward exhibit empty p states. These results, which support earlier models,[7,8] proposed for the reconstruction of Si surfaces, allow one to expect the vacancy in the outward moving atoms to induce stronger effects on the surface reconstruction than the vacancy in the atoms that move inward. This is because the former case corresponds to a vacancy in occupied orbitals. Thus, if these orbitals are removed, as a result of the creation of the vacancy, the electrons from the neighboring atoms that were present in the doubly occupied s state now return to their parent atoms and seek other bonding configurations.

We have performed exhaustive tests to check for the convergence of our results. In particular, the subspace used is one of the largest employed in order to keep the calculations within the available computational resources. While the short-range nature of the interactions gave us confidence in our choice of the number of layers in the z direction, the size along the surface plane had to be tested further for adequacy. With this in mind, we first tested for the convergence of our results for the reconstructed geometry by employing subspaces of various surface sizes, keeping the number of z layers the same. Our tests included subspace sizes of 16–28 atoms. The values of ϕ, $\triangle y$, and $\triangle z$ were found to change from 27.2°, 0.38 Å, and 0.10 Å to 27.6°, 0.35 Å, and 0.13 Å, respectively, in going from 16-atom to 28-atom subspace clusters. In a subsequent test we investigated also the accuracy of our results by checking the projected electron DOS before and after the relaxation. It was found that for the central surface atoms of our 28-atom subspace cluster, the molecular-dynamics relaxation removed, as expected,[6] all the electronic gap states associated with the Si dangling bonds for the unreconstructed Si(110) surface. This test is a significant check of our method, ensuring that the present scheme provides a realistic model to study the surface-adatom bonding interactions.

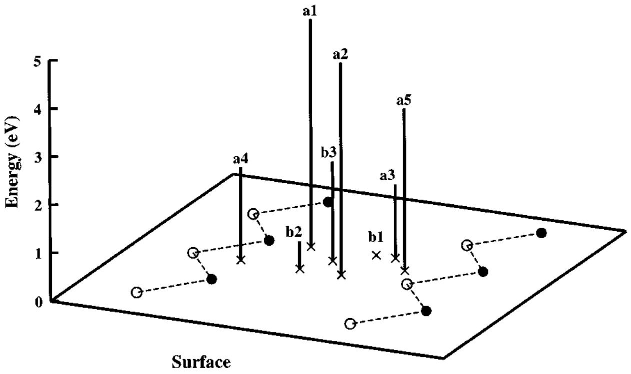

FIG. 2. Two-dimensional projection of the surface layer of the 1×1 reconstructed Si(110) surface with various positions of a single Si adatom sites. The open circles denote substrate atoms that moved inward upon relaxation, while the solid circles denote atoms that moved outward on relaxation. The vertical bars denote relative energies for these sites. Sites labeled ax ($x=1,5$) denote bonding positions in which Si adatoms bond only to a single surface zigzag chain. Sites labeled bx ($x=1,3$) correspond to adatom bonding positions where Si forms bonds to substrate atoms belonging to two neighboring zigzag chains. The most stable position [shown in Fig. 1(c)] for the adatom is site b1.

Having described the bare Si(110) surface to a good approximation, we next proceed with the problem of the interaction of Si adatoms with this surface. We have investigated several chemisorption sites for an isolated Si atom by placing it initially at a distance of about 2.5 Å above the surface plane, in various positions of both the 1×1 and 2×1 reconstructed Si(110) surfaces to determine the most stable configuration for chemisorption. Starting from any of these initial positions, the external Si atom always finds an equilibrium site close to it, this position being a local energy minimum for the system. The relative energies and positions of the equilibrium bonding configurations of the Si adatom on the 1×1 reconstructed Si(110) surface are shown in Fig. 2. All equilibrium sites are above the outer atomic plane of the substrate. Similarly, several equilibrium bonding configurations were also obtained for Si adatoms on the 2×1 reconstructed surface, which also included an interstitial site with the adatom bonding to six substrate atoms. It is worth noting that for the bonding sites studied, the Si adatom always changes the reconstruction as it bonds to the substrate. Both the coordination number of the adatom and the removal of surface reconstruction due to its presence were found to correlate with the charge state of the adatom. The net charge of the Si adatom is found to depend on the bonding positions, ranging from ±0.30 electrons (at the most stable bonding site) to −1.04 electrons (at the less stable sites). Thus the type of bonding between the adatom and the surface may change from covalent to ionic as the adatom moves on the surface. The Si adatom bonds above the reconstructed surface at heights that vary from 0.6 to 2.0 Å. At its most stable position [b1 on 1×1 Si(110)], the Si adatom bonds about 1.0 Å from the top substrate atomic plane [Fig. 1(c)]. At this position, the adatom loses 0.31 electrons to the substrate with which it makes four bonds. Three of the bonds are developed with three consecutive substrate atoms belonging to the same zigzag chain. Two of these bonds (of lengths 2.45 and 2.48 Å) are formed with the chain atoms that moved inward upon relaxation, while the third bond (of length 2.72 Å) is formed with the chain atom that moved outward upon relaxation. The fourth bond (of length 2.55 Å) is formed with a substrate atom that moves outward on reconstruction but belonging to a neighboring chain [see Fig. 1(c)]. Thus we find the same bonding tendency for the adatom when forming bonds with distant substrate atoms as was also found in the case of the chemisorption of a Si adatom on the Si(100) surface.[9]

In summary, we have presented an exhaustive investigation of the surface reconstruction of the Si(110) surface and its interaction with Si atoms using a TBMD scheme. Our results support the rotational model for the surface reconstruction and rule out the dimer model for its description. Upon chemisorption of Si adatoms, the reconstruction of the Si(110) surface is removed. Our calculational results are in agreement with results of other theoretical works and with experiment.

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[1] F. Jona, IBM J. Res. Dev. **9**, 375 (1965).

[2] B. Z. Olshanetsky and A. A. Shklyaev, Surf. Sci. **67**, 581 (1977).

[3] Y. Yamamoto, Phys. Rev. B **50**, 8534 (1994); Jpn. J. Appl. Phys. 1 **31**, 2544 (1992); Y. Yamamoto, S. Ino, and T. Ichikawa, Jpn. J. Appl. Phys. 2, Lett. **4**, L331 (1986).

[4] T. Ichinocawa, H. Ampo, S. Miura, and A. Tamura, Phys. Rev. B **31**, 5183 (1985).

[5] H. Ampo, S. Miura, K. Kato, Y. Ohkawa, and A. Tamura, Phys. Rev. B **34**, 2329 (1986).

[6] B. A. Nesterenko and A. I. Shkrebtii, Surf. Sci. **171**, 495 (1986);

213, 309 (1989); **247**, 188 (1991); Appl. Surf. Sci. **33/34**, 21 (1988).

[7] W. Harrison, in *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980).

[8] D. J. Chadi, Phys. Rev. B **19**, 2074 (1978); Phys. Rev. Lett. **41**, 1062 (1978).

[9] G. Brocks, P. J. Kelly, and R. Car, Phys. Rev. Lett. **66**, 1729 (1991).

[10] G. Brocks and P. J. Kelly, Phys. Rev. Lett. **76**, 2362 (1996).

[11] C. W. Oh, E. Kim, and Y. H. Lee, Phys. Rev. Lett. **76**, 776 (1996).

[12] M. Menon and R. E. Allen, Phys. Rev. B **33**, 7099 (1986); **38**, 6196 (1988).

[13] M. Menon, J. Connolly, N. Lathiotakis, and A. N. Andriotis, Phys. Rev. B **50**, 8903 (1994); N. N. Lathiotakis, A. N. Andriotis, M. Menon, and J. Connolly, Europhys. Lett. **29**, 135 (1995); J. Chem. Phys. **104**, 992 (1996).

[14] A. N. Andriotis, N. Lathiotakis, and M. Menon, Chem. Phys. Lett. **260**, 15 (1996); Europhys. Lett. **36**, 37 (1996).

[15] J. E. Inglesfield, J. Phys. C **14**, 3975 (1981).

[16] G. A. Baraff and M. Schluter, J. Phys. C **19**, 4383 (1986).

[17] A. N. Andriotis, Europhys. Lett. **17**, 349 (1992); J. Phys. Condens. Matter. **2**, 1021 (1990).

[18] A. D. Mistriotis, A. Zdetsis, G. E. Froudakis, and M. Menon, J. Phys. Condens. Matter **5**, 6183 (1993).

[19] K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. **89**, 2219 (1988).

[20] U. Rothlisberger, W. Andreoni, and M. Parrinello, Phys. Rev. Lett. **72**, 665 (1994).