Ab Initio Total-Energy Calculations for Extremely Large Systems: Application to the Takayanagi Reconstruction of Si(111)

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We have implemented a set of total-energy pseudopotential codes on a parallel computer which allows calculations to be performed for systems containing many hundreds of atoms in the unit cell. Using these codes we have calculated the total energies and structures of the 3×3, 5×5, and 7×7 Takayanagi reconstructions of the (111) surface of silicon. We find that the 7×7 structure minimizes the surface energy and observe structural trends across the series which can be correlated with the degree of charge transfer between the dangling bonds on the adatoms and rest atoms.

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The Takayanagi reconstruction [1] is observed on the (111) surface of silicon, silicon-germanium alloys [2], and strained (compressed) germanium [3]. It is the most complex reconstruction so far observed on any semiconductor surface. The extremely large area and vertical extent of the observed reconstruction present a formidable challenge to a fully *ab initio* calculation of the total energy and structural properties of this surface which place such an investigation beyond the power of conventional supercomputers. By implementing a set of total-energy pseudopotential codes on a parallel supercomputer (a 64-node Meiko i860 Computing Surface) we have performed a fully *ab initio* investigation of a series of Takayanagi reconstructions, namely, the 3×3, 5×5, and 7×7 structures. Technical details of the implementation of the codes will be presented elsewhere [4].

The structure of the Si(111) surface has been a subject of continued interest since the first observation of a 7×7 reconstruction in 1959 [5]. A large number of models have been proposed for the structure but only the model proposed by Takayanagi *et al.* [1] is consistent with all the available experimental measurements. The Takayanagi model incorporates the following features: (i) dimerization of second-layer atoms, (ii) adatoms, and (iii) a stacking fault between the first and second layers of atoms over one-half of the unit cell. Hence, the Takayanagi structure is commonly referred to as the DAS structure. Previous theoretical investigations of the DAS model based on qualitative arguments [6], semiempirical tight-binding calculations [7], and *ab initio* calculations for the 3×3 model [8] provided a qualitative understanding of the role of the dimer-row domain walls [6] and adatoms [8] in stabilizing the DAS model. Two recent *ab initio* plane-wave pseudopotential calculations have been performed to determine the electronic structures of the Si(111) 5×5 and 7×7 reconstructions [9]. However, these calculations used too small a cutoff energy for the plane-wave basis set to allow atomic relaxation or for surface energies to be calculated.

The main results of our calculations are as follows: (1) The calculated energies for the relaxed structures predict the 7×7 Takayanagi structure to be the most energetically favorable and the 3×3 structure to be the least favorable. (2) There is a systematic reduction in the length of the dimers and the height of the adatoms and rest atoms across the series of reconstructions. (3) These structural changes can be explained by an increasing degree of charge transfer from the adatoms to the rest atoms.

The number of dimers, adatoms, rest atoms, corner-hole atoms, and stacking faults per unit cell in the 3×3, 5×5, and 7×7 Takayanagi structures are summarized in Table I. The table also shows the number of atoms per unit cell used for the calculations. In our calculations the total-energy functional is minimized with respect to both the plane-wave coefficients of the occupied orbitals and the ionic degrees of freedom. The electronic minimization is performed using the conjugate-gradient technique [10] and a steepest-descent algorithm was used for the ionic relaxation. Electron-electron interactions were included in the local-density approximation of density-functional theory. We used Perdew and Zunger's parametrization [11] of the exchange-correlation energy. Kerker pseudopotentials [12] were applied in the Kleinman-Bylander form [13], with the *s*-wave component treated as local, retaining three *p* and five *d* projectors using a real-space projection technique [14] which significantly increases the efficiency of large-scale calcu-

TABLE I. Number of characteristic features in the Takayanagi DAS structures. The symbol $\frac{1}{2}$ means a stacking fault over one-half of the unit cell.

	Dimer	Adatom	Stacking fault	Rest atom	Corner hole	Atoms in supercell
3×3	3	2	$\frac{1}{2}$	0	1	68
5×5	6	6	$\frac{1}{2}$	2	1	200
7×7	9	12	$\frac{1}{2}$	6	1	400

TABLE II. Results of the surface energy calculations.

	3×3	5×5	7×7
Energy per unit cell (eV)	10.765	29.205	56.509
Energy per surface atom (eV)	1.196	1.168	1.153

lations. In our calculations for the 5×5 and 7×7 reconstruction the unit cell is large enough for the Brillouin zone (BZ) to be sampled by a single k point [15]. The calculation for the 3×3 structure was performed using four k points to provide a comparable accuracy in the BZ sampling. The electronic wave functions were expanded in a plane-wave basis set with an energy cutoff of 7 Ry. This value has been shown to provide an accurate description of electronic and structural properties of silicon surfaces [16]. The calculations were performed using eight-layer-thick slabs in which the central two layers of atoms were kept fixed to simulate the bulk crystal termination of the surface. The length of the unit cell normal to the surface was 8 times the double-layer spacing in the [111] direction of the bulk crystal. The dimensions of the cell were fixed according to the experimental bulk lattice parameter. The calculations were terminated when the forces on all the ions were smaller than 0.1 eV/Å.

The results of the calculations for the surface energy [17] are shown in Table II. The 7×7 DAS structure has the lowest surface energy and the 5×5 and 3×3 structures are decreasingly stable. However, it can be seen that the changes in the surface energies are saturating towards the 7×7 structure, which indicates that the 9×9 and larger structures may be energetically unfavorable.

We now turn to an analysis of the structural properties of the reconstructions. The values of the most important structural parameters of the DAS reconstructions are shown in Table III. It can be seen that the adatoms move inward towards the ideal tetrahedral positions across the series from 3×3 to 7×7 and the triangles of first-layer atoms underneath the adatoms expand. The entire first-layer islands tend to expand across the series of reconstructions and we observe an asymmetry between the two halves of the unit cell such that the unfaulted half is slightly larger. The rest atoms also move in towards the ideal tetrahedral positions going from the 5×5 to 7×7 structure. There is a reduction in the average length of the dimers across the series from 3×3 to 7×7 which ap-

TABLE III. Structural parameters in the DAS reconstructions: average height of the adatoms from the ideal tetrahedral position $\bar{\Delta}_{aa}$, average length of the side of the triangle of first-layer atoms beneath the adatoms $\bar{l}_{\Delta}$, average normalized area of entire triangular first-layer islands $\bar{S}_{\Delta}$, average height of the rest atoms from the ideal tetrahedral position $\bar{\Delta}_{da11}$, average length of the dimers $\bar{l}_d$, and average distance of the dimer atoms from the first-layer atoms $\bar{l}_{d\text{-}a11}$.

	$\bar{\Delta}_{aa}$ (Å)	$\bar{l}_{\Delta}$ (Å)	$\bar{S}_{\Delta}$ (Å^2)	$\bar{\Delta}_{da11}$ (Å)	$\bar{l}_d$ (Å)	$\bar{l}_{d\text{-}a11}$ (Å)
3×3	0.554	3.566	5.506	···	2.455	2.487
5×5	0.521	3.600	6.064	0.226	2.451	2.448
7×7	0.508	3.618	6.252	0.201	2.442	2.431

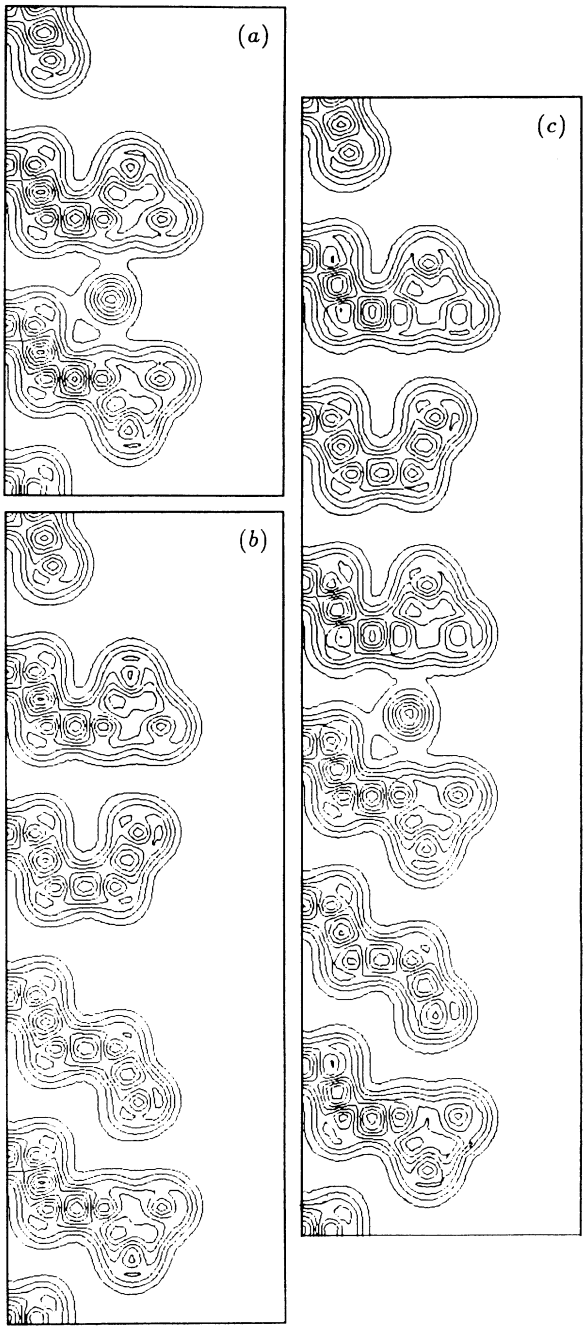

FIG. 1. Contour plots of the charge density along the long diagonal in the unit cell of (a) 3×3, (b) 5×5, and (c) 7×7 Takayanagi structures.

pears not to saturate at the 7×7 structure. However, this is caused by the different behavior of dimers in the middle of the cell edges which are considerably shorter (2.427 Å) than the dimers adjacent to the corner holes (2.449 Å). The reduction in the length of dimers on moving from the 3×3 to the 7×7 structure is accompanied by a decrease in the lengths of the bonds from the dimers to the first-layer atoms. The height of the atoms in the second and third layers is strongly affected by the adatoms and rest atoms. The second- and third-layer atoms directly beneath the adatoms move towards the substrate, whereas the second-layer atoms bonded to the rest atoms move upwards. In all the DAS reconstructions the structure of the corner holes shows very little variation, which suggests that the corner holes do not play a significant role in stabilizing any particular member of the series of reconstructions. The in-plane positions of the atoms in the 7×7 have been extracted from x-ray measurements by Robinson *et al.* [18]. With the exception of the lengths of the dimer bonds we find good agreement with their values. However, our value for the average length of the dimer bonds, 2.442 Å, is significantly less than their value of 2.49 Å. As can be seen from Table III, the changes in the structural parameters appear to be saturating at the 7×7 structure, which again indicates that larger unit cells may not be energetically favorable.

Finally we analyze the self-consistent valence-electronic-charge densities $\rho(\mathbf{r})$. In Fig. 1 we show $\rho(\mathbf{r})$ along the long diagonals of the unit cells. The main trend we observe is an increasing transfer of charge from dangling bonds on the adatoms to the dangling bonds on the rest atoms across the series from 3×3 to 7×7, which is to be expected from the increasing ratio of rest atoms to adatoms. The decrease in the height of the adatoms can be explained by the reduction in the charge in the dangling bonds on these atoms and the consequent tendency towards sp^2 rather than sp^3 hybridization. The charge density in the dangling bonds on the rest atoms is smaller in the 7×7 reconstruction than in the 5×5 because of the higher ratio of rest atoms to adatoms. This explains the reduction in the height of the rest atoms on moving from the 5×5 to the 7×7 structure. We observe interesting variations between the faulted and unfaulted halves of the unit cell. In the 3×3 and 5×5 reconstructions the charge densities on the adatoms in the two halves of the unit cell are broadly similar. Although, in the case of the 5×5 structure the larger charge density on the rest atom in the unfaulted half of the cell suggests that the charge transfer from the adatoms is larger in this region. In the 7×7 reconstruction the charge densities in the two halves of the unit cell are very different. In the unfaulted half of the cell the charge transfer from the adatoms is significantly larger than in the 5×5 structure and it is the same for all the adatoms. However, in the faulted half of the unit cell the adatoms adjacent to the corner hole have more charge than the adatoms in the middle of the cell and both types of adatom have more charge than the adatoms in the unfaulted half of the cell. These results are consistent with scanning tunneling microscope images of the surface [19]. In Fig. 2 we show $\rho(\mathbf{r})$ in the plane containing the dimers and note the tendency to form stronger covalent bonds across the series 3×3 to 7×7.

In conclusion, we have presented the first fully *ab initio* calculations of the energies and structures of the 3×3, 5×5, and 7×7 Takayanagi reconstructions of the Si(111) surface. Our calculations predict the 7×7 to be the most energetically stable structure and the 3×3 to be the least stable structure. Structural analysis revealed a systematic reduction in the length of dimers and the height of the adatoms and rest atoms across the series of reconstructions, which is correlated with the charge in the dangling bonds on the adatoms and rest atoms. Both the energy differences and the structural parameters show signs of saturation at the 7×7 structure, thus indicating that larger Takayanagi structures may not be energetically favorable. Analysis of other properties of these reconstructions, such as surface states, as well as dynamical simulations and analysis of adatom vibrations are now underway.

Although these calculations involve many hundreds of atoms in the unit cell they have been carried out on a

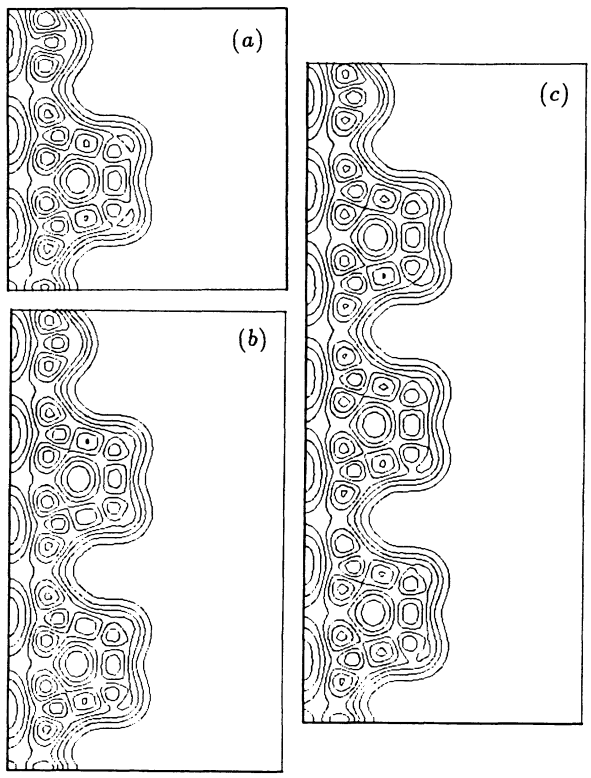

FIG. 2. Contour plots of the charge density along the dimers in (a) 3×3, (b) 5×5, and (c) 7×7 Takayanagi structures.

parallel computer with only 64 computing nodes. The strategy used to run these codes on the parallel machine can be applied to arbitrary large numbers of computing nodes so that with a larger machine it will be possible to perform total-energy pseudopotential calculations for systems containing thousands of atoms in the unit cell.

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