# *Ab Initio* Theory of the Si(111)-(7×7) Surface Reconstruction: A Challenge for Massively Parallel Computation

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An *ab initio* investigation of the Si(111)-(7×7) surface reconstruction is undertaken using the state of the art in massively parallel computation. Calculations of the total energy of an ~700 effective-atom supercell are performed to determine (1) the fully relaxed atomic geometry, (2) the scanning tunneling microscope images as a function of bias voltage, and (3) the energy difference between the (7×7) and the (2×1) reconstructions. The (7×7) reconstruction is found to be energetically favorable to the (2×1) surface by 60 meV per (1×1) unit cell.

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The (7×7) reconstruction of Si(111) is perhaps the most complex and widely studied surface of a solid. Since its discovery through low-energy electron diffraction (LEED) more than thirty years ago [1], an enormous amount of effort has been expended to elucidate the properties of this important surface [2–11]. Based on this work, it is now generally accepted that the geometry of the (7×7) reconstruction is described by a dimer-adatom-stacking-fault (DAS) model as proposed by Takayanagi *et al.* [5]. The complexity of this geometry, however, has defied any complete and realistic theoretical treatment of its properties. The only progress that could be made theoretically was by isolating and modeling bits and pieces of the surface. The only attempt at a complete work used an empirical tight-binding model to study the Si(111)-(7×7) reconstruction in a supercell geometry with 196 atoms [10]. In this Letter, we exploit the power of the state of the art in parallel computation to demonstrate the feasibility of performing *ab initio* calculations with supercells approaching 1000 atoms. Specifically, we

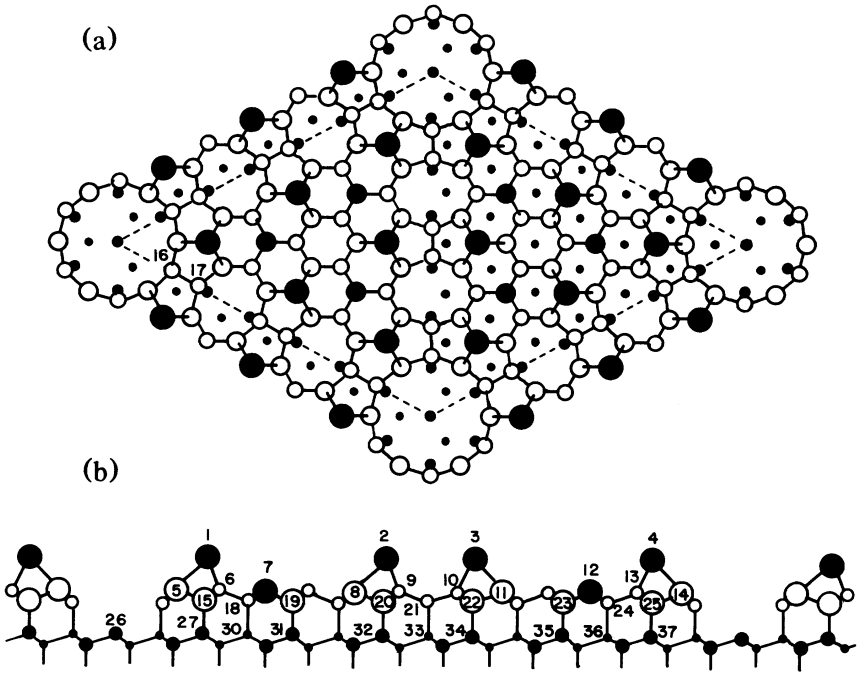


FIG. 1. (a) Top view of the DAS model for the Si(111)-(7×7) surface reconstruction. The (7×7) unit cell is outlined. Atoms at increasing distances from the surface are indicated by circles of decreasing size. The large solid circles denote the twelve adatoms. The smaller solid circles represent the rest atoms. The faulted half of the unit cell is on the left. Small open circles denote the dimers, while small solid circles and dots represent atoms in the unreconstructed layers. (b) Side view. Atoms on the lattice plane along the long diagonal of the surface unit cell are shown with larger circles than those behind them. The numbers label the 37 unique atoms in the four-layer slab. All others are related by symmetry operations.

have performed the first *ab initio* calculation of the Si(111)-(7×7) reconstruction using a supercell geometry with 700 effective atoms. These calculations predict the fully relaxed atomic geometry of this system, allow construction of theoretical scanning tunneling microscope (STM) images as a function of bias voltages, and predict the energy difference between the (7×7) and (2×1) reconstructions.

The DAS model for the Si(111)-(7×7) surface reconstruction is shown in Fig. 1. The unit-cell boundary is outlined by a dashed line. The largest solid circles denote the twelve adatoms. The smaller solid circles denote six rest atoms that lie one layer below the surface and are threefold coordinated. There is also a single corner hole in each unit cell. Together, these 19 atoms account for the 19 unbonded electrons on the reconstructed surface. The smallest solid circles denote the fourth layer of atoms below the surface on the unfaulted half of the unit cell. Nine dimers are present two layers below the surface. One dimer is labeled by atoms with the numbers 16 and 17. The side view shows that the stacking sequence in the right half of the unit is the same as in bulk Si while the stacking sequence in the left half is faulted.

Our model system consists of a supercell with a slab geometry containing vacuum on both sides. Periodic boundary conditions are applied in all directions. The slab contains the adatom layer and four surface layers shown in Fig. 1(b) plus a mirror image reflection in the vertical direction. Thus the supercell consists of eight layers of atoms with adatom layers on both slab surfaces and a region of 10 Å of vacuum. The 400 silicon atoms and the vacuum layer make this supercell equivalent to a 700-atom system. Unit-cell dimensions are 22 Å×22 Å×26 Å.

We used the *ab initio* molecular-dynamics scheme for calculating total energies and performing simulated quenching [12,13]. To compute the total energy, we used the local-density approximation in the Perdew-Zunger [14] form of the exchange-correlation energy, and a norm-conserving nonlocal Kleinman-Bylander pseudopotential [15,16]. Because of the large size of our unit cell, only the Γ point of the Brillouin zone was used. To check for convergence, we performed the calculation at 4, 5, 6, and 8 Ry. The 6-Ry calculation requires a basis set size of about 26000 plane waves per unit cell.

All atoms were allowed to move freely except the innermost layer, which was frozen in its bulk position. Thus our model of the surface includes the relaxation of three surface layers in addition to the adatom layer. The atoms were assumed to be in their fully relaxed positions when the forces on the ions were converged to 0.15 eV/Å.

The memory requirement for the wave functions and associated arrays exceeds 60 megawords. The large size of this system makes a massively parallel supercomputer desirable. We used a Thinking Machines CM-2. Our 6-Ry calculation employed an array of 16384 one-bit processors. The processor array ran at an effective rate of 600 megaflops, enabling this system to be studied with *ab initio* techniques within several hundred hours. In implementing the calculation on a parallel computer, we spread the 26000 plane waves across the parallel processing units. Calculations on a given band were performed in parallel. Each band was processed sequentially. The

TABLE I. Relaxed atomic positions for the adatom layer and the first three surface layers for the *ab initio* (7×7) calculation. The coordinate system is the same as in Ref. [10]. All reduced coordinates $(X, Y, Z)$ are with respect to the Cartesian system indicated in Fig. 1, where the $x$ axis is along the cubic [110] direction, and the $y$ axis is along the [111] outward normal to the surface. The actual atomic coordinates $(x,y,z)$ are related to $(X,Y,Z)$ by the scaling relations $x=aX$, $y=aY/\sqrt{3}$, $z=aZ/\sqrt{24}$, where $a\approx 3.85$ Å is the (1×1) surface hexagonal lattice constant.

| | Atom | $X$ | $Y$ | $Z$ |
|---|---|---|---|---|
| Adatoms | 1 | 1.500 | 1.500 | 1.662 |
| | 2 | 4.492 | 4.491 | 1.594 |
| | 3 | 6.002 | 6.002 | 1.555 |
| | 4 | 9.005 | 9.005 | 1.603 |
| First-layer atoms | 5 | 1.033 | 1.033 | −0.057 |
| | 6 | 1.958 | 0.993 | −0.058 |
| | 7 | 2.481 | 2.481 | 0.348 |
| | 8 | 4.021 | 4.022 | −0.155 |
| | 9 | 4.974 | 4.050 | −0.099 |
| | 10 | 5.980 | 5.057 | −0.135 |
| | 11 | 6.478 | 6.478 | −0.163 |
| | 12 | 8.019 | 8.019 | 0.345 |
| | 13 | 9.029 | 8.059 | −0.104 |
| | 14 | 9.472 | 9.472 | −0.111 |
| Second-layer atoms | 15 | 1.504 | 1.504 | −1.512 |
| | 16 | 1.162 | 0.006 | −1.057 |
| | 17 | 1.800 | 0.007 | −1.042 |
| | 18 | 2.492 | 1.499 | −0.867 |
| | 19 | 2.969 | 2.969 | −0.863 |
| | 20 | 4.494 | 4.495 | −1.561 |
| | 21 | 5.403 | 4.780 | −1.046 |
| | 22 | 6.004 | 6.004 | −1.567 |
| | 23 | 7.532 | 7.532 | −0.871 |
| | 24 | 8.505 | 7.510 | −0.874 |
| | 25 | 8.998 | 8.998 | −1.537 |
| Third-layer atoms | 26 | 0.001 | 0.001 | −3.986 |
| | 27 | 1.500 | 1.500 | −4.416 |
| | 28 | 1.006 | −0.002 | −3.989 |
| | 29 | 1.990 | 0.000 | −3.964 |
| | 30 | 2.499 | 1.499 | −3.946 |
| | 31 | 2.997 | 2.997 | −3.951 |
| | 32 | 4.499 | 4.499 | −4.460 |
| | 33 | 5.496 | 4.512 | −3.973 |
| | 34 | 5.999 | 5.999 | −4.440 |
| | 35 | 7.497 | 7.497 | −3.933 |
| | 36 | 8.505 | 7.496 | −3.930 |
| | 37 | 9.001 | 9.001 | −4.414 |

parts of the calculation requiring a three-dimensional real-space or reciprocal-space grid were also spread across the parallel processing array. The calculation performance was limited by interprocessor communication during sums across the processing array, fast Fourier transforms, and unpacking plane waves into a full reciprocal-space grid.

Table I shows the relaxed ionic positions. The coordinate system is the same as that of Ref. [10]. The computed positions in the surface plane are nearly identical with those from the tight-binding calculations. The most significant differences involve expansion of the surface layers away from the bulk layer. Compared to the tight-binding calculations, the adatoms move $\sim$0.03 Å away from the bulk layer. The rest atoms move $\sim$0.02 Å toward the bulk layer. Most of the remaining atoms move $\sim$0.05 Å away from the bulk layer. However, atoms directly below adatoms move only $\sim$0.03 Å resulting in a more distorted adatom configuration. The atoms two layers directly below move the most compared to the tight-binding calculations, relaxing $\sim$0.10 Å away from the bulk layer. The relative heights of adatoms 1, 2, 3, and 4 are 0.085, 0.031, 0.000, and 0.038 Å, respectively. Experimental LEED values from Ref. [9] are 0.120, 0.080, 0.0, and 0.040.

Having generated the electronic wave functions in our pseudopotential calculation, we proceeded to make theoretical STM figures. In Fig. 2, we compare the theoretical results (top) with corresponding experiments [17] at a tip voltage of 2 V (bottom) for both occupied and unoccupied states. The theoretical STM images were generated using the method of Tersoff and Hamann [18].

The theoretical STM probe was placed 3.8 Å above the surface adatom layer. The probe height is limited by the presence of a second surface layer above the probe due to the periodic replication of the unit cell. The theoretical grey scale was matched to the experimental grey scale at the tops of the adatoms and the bottoms of the corner holes, and linearly interpolated in between. Experiments show a variation of 2–3 Å corresponding to this scale. The corresponding theoretical variation is 5 Å. Depths

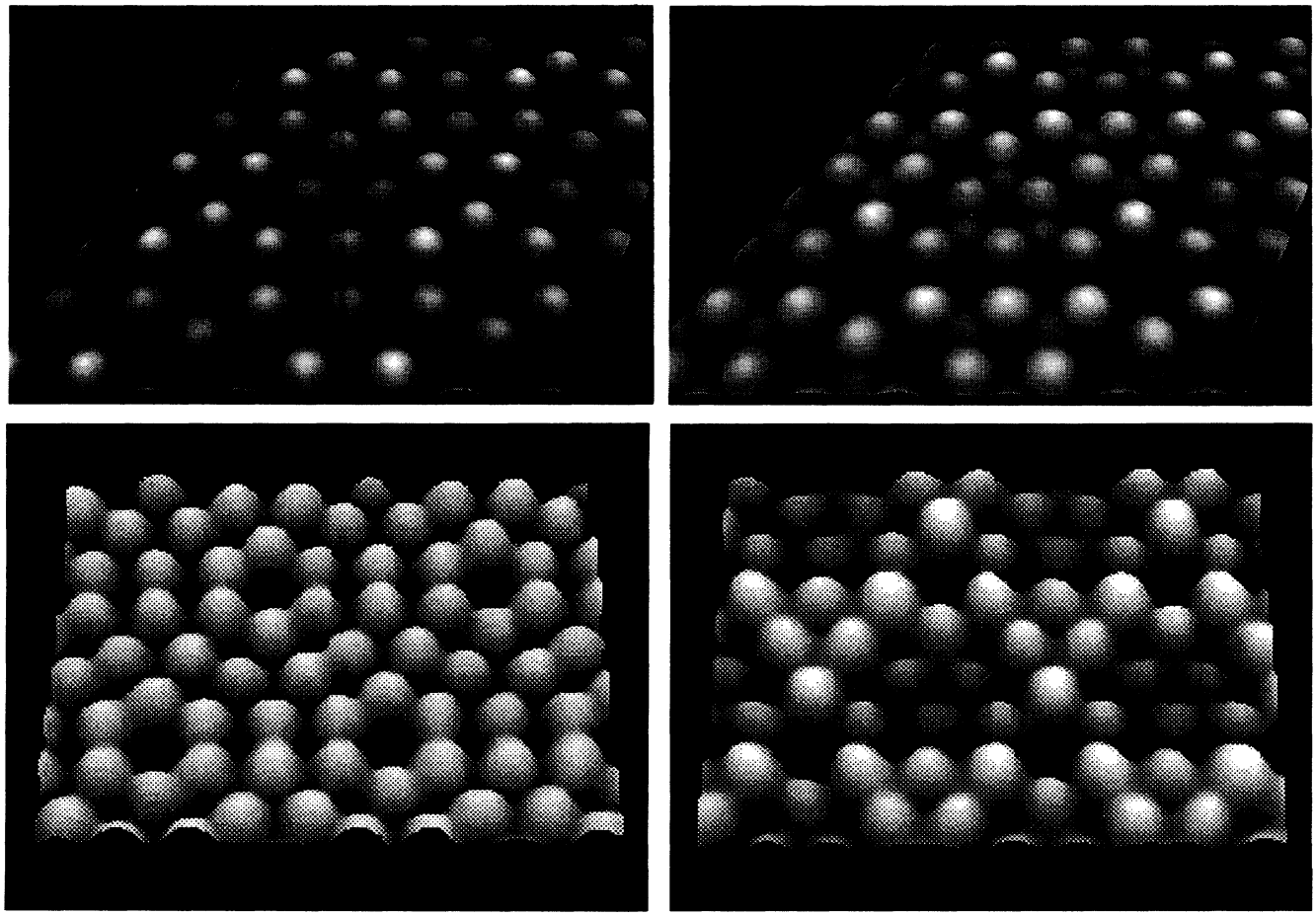

FIG. 2. STM images of the Si(111)-(7×7) surface reconstruction based on the results of this calculation (top panels), and the experimental results of Avouris and Wolkow [17] (bottom panels). Shown are unoccupied (left panel) and occupied (right panel) state contributions. The determination of the grey scale in the top panels is described in the text.

greater than 3 Å are set to minimum intensity in order to match the experimental grey scale.

The most fundamentally interesting part of this calculation is the comparison of formation energies of the (7×7) reconstruction and the (2×1) surface [19]. Cleavage of Si to create the (111) surface results in a (2×1) metastable structure. This surface must then be annealed to generate the stable (7×7) structure. To compute the energy of the (2×1) surface, we used sixteen **k** points in the irreducible Brillouin zone that correspond exactly to the **k** point Γ in the (7×7) unit cell. Using an 8-Ry cutoff energy, we find that the (7×7) reconstruction is energetically favorable over the metastable (2×1) surface by 60 meV per (1×1) cell. Our absolute values are 1.179 eV for the (7×7) surface and 1.239 eV for the (2×1). Calculations at 4, 5, 6, and 8 Ry yield energy differences of 0.001, 0.030, 0.044, and 0.060 eV per cell. This shows that the energy is satisfactorily converged.

In conclusion, we have performed an *ab initio* investigation of the electronic and geometric structure of the Si(111)-(7×7) surface reconstruction. These calculations are made possible because of the considerable computational power associated with massively parallel architectures. The calculations elevate *ab initio* investigations to a new echelon and demonstrate that studies of complex material systems with supercells containing nearly an order of magnitude more atoms than previously possible are now feasible.

We are very grateful to Dr. In-Whan Lyo for providing unpublished STM images from the work of Ref. [17] which led to Fig. 2. We should like to thank T. Arias, R. Meade, A. Rappe, and J. Wang for many helpful discussions. D. Philimore and J. Reardon provided assistance with the Connection Machine. This work was supported in part by ONR Contract No. N00014-86-K-0158 and JSEP Contract No. DAAL-03-86-K-0002. The (7×7) calculations were performed on Connection Machines at the Pittsburgh and Los Alamos Supercomputer Centers. The (2×1) calculations were performed on the Cray YMP at the San Diego Supercomputer Center.

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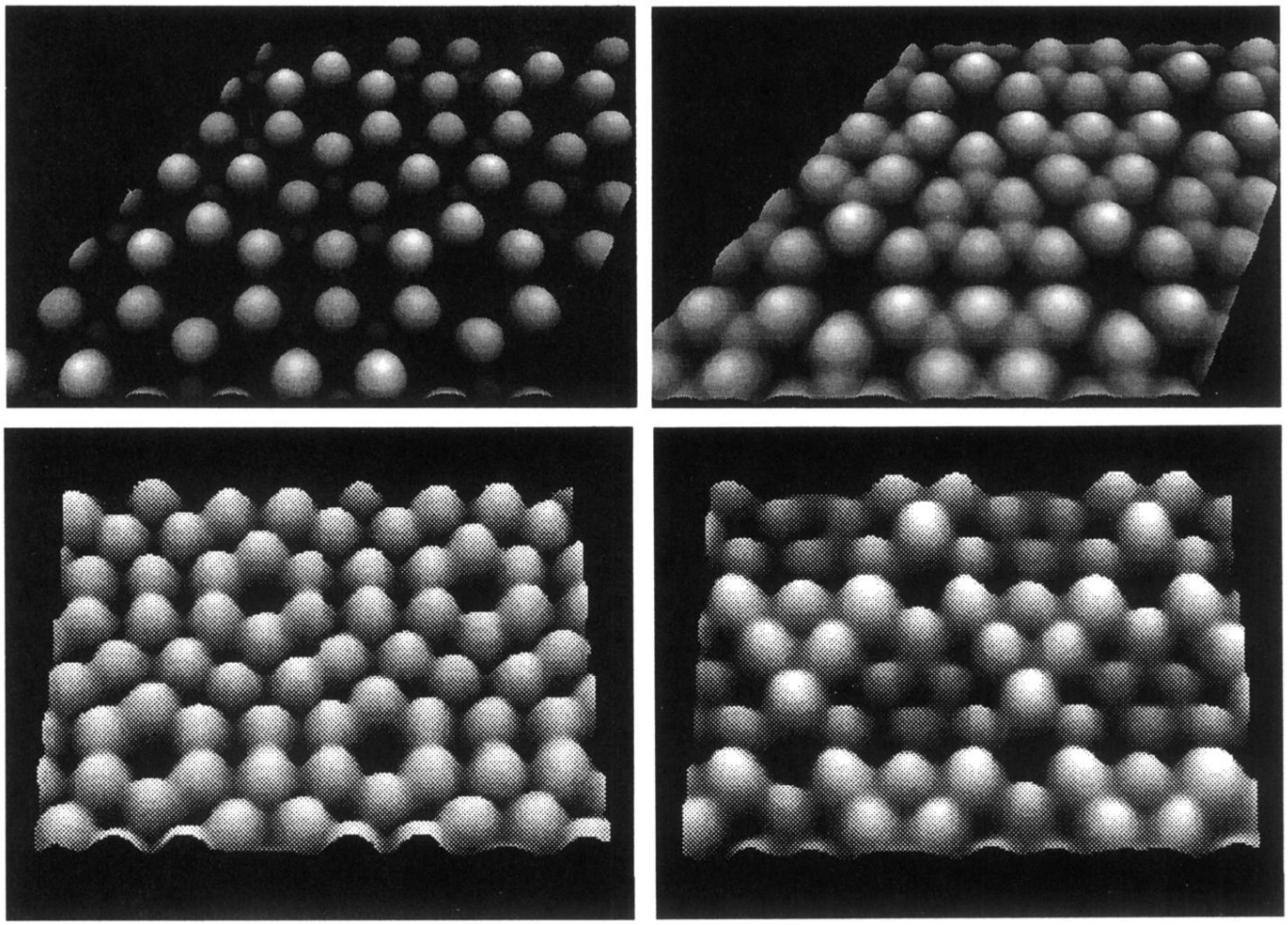

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