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High-order reconstructions of the Ge(100) surface

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We have performed *ab initio* density-functional calculations of total energies of the Ge(100) surface to compare the ground states of (2×1), $c(4\times2)$, $p(2\times2)$, and $p(4\times1)$ symmetry dimer reconstructions. We find that $p(2\times2)$ and $c(4\times2)$ are the lowest-energy reconstructions and are nearly degenerate in energy. From these *ab initio* total energies, we compute the coupling constants for a model Hamiltonian for the surface and predict the phase-transition temperature from either an ordered $c(4\times2)$ or $p(2\times2)$ state to a disordered buckled $b(2\times1)$ state.

I. INTRODUCTION

At the surface of a solid the three-dimensional periodicity of the crystal no longer exists and the surface atoms relax from what would be their bulk or "ideal" positions. Because the bonding in semiconductors, such as silicon and germanium, is both strong and highly directional, this relaxation can be quite extensive as the surface atoms move to eliminate one or more of their dangling bonds. One such semiconductor surface that has been studied for a long time is the (100) surface of germanium and the related silicon (100) surface.[1-11] Many different structures, such as symmetric dimer,[1] asymmetric dimer,[2] vacancy,[3] and conjugated chain,[4] have been proposed as the ground state for either of these surfaces. An additional and highly interesting facet of this problem is the possibility of different symmetries existing for each type of structure. In fact, most of the experimental investigation, such as He scattering,[8,9] x-ray and low-energy electron diffraction (LEED),[9,10] and electron emission[10] of the Si(100) and Ge(100) surfaces, has been to determine the symmetry of the reconstruction rather than the structure. Only with the relatively recent advent of scanning tunneling microscopy (STM) can experiment determine directly the structure of the surface reconstruction.[5,6] In this paper we present the results of an *ab initio* theoretical investigation of the energetics of one family of dimer reconstructions of the Ge(100) surface. In the following four sections we (1) describe the calculational procedure we used, including a brief description of quantum molecular dynamics, (2) give a description of our results and a comparison to experiments, (3) predict the temperature of a phase transition from one symmetry dimer reconstruction to another, and (4) finally present our conclusions.

II. CALCULATIONAL PROCEDURE

We computed and minimized the total energy of the four members of the (2×1) family of buckled dimer reconstructions. The (2×1) family is characterized by rows of dimers as illustrated in Fig. 1. The four members are the buckled (2×1)-$b(2\times1)$ shown in Fig. 1(a), the centered (4×2)-$c(4\times2)$, shown in Fig. 1(b), the primitive (4×1)-$p(4\times1)$, shown in Fig. 1(c) and, lastly, the primitive (2×2)-$p(2\times2)$, shown in Fig. 1(d). The members differ in the arrangement of "up" and "down" dimers on the (2×1) backbone both in and perpendicular to the dimer rows.

To model the surface, we used a slab geometry of eight layers, a vacuum region of 9.8 Å and periodic boundary conditions. Thus, we have two surfaces in our unit cell. We froze the innermost two layers and allowed the outermost three layers on each side of the slab to relax. We imposed inversion symmetry to increase the tractibility of the computation. Our previous work[7] showed that this restriction does not affect the results of the calculation.

We computed the total energy of the slab using an *ab initio*, norm-conserving local pseudopotential[12] parametrized as in Ref. 7 and the local-density approximation within the density-functional theory. We used the Ceperley-Alder[13] form of the Perdew-Zunger[14] form of the exchange-correlation potential. We expanded the electronic states in terms of plane waves, using an energy cutoff of 7.28 Ry (5652 plane waves). To check the accuracy of the resulting total energies, we extended the energy cutoff to 8, 9, and 11 Ry and the total-energy differences were converged to 3 meV/dimer. We used the two Monkhorst-Pack special k points $(\frac{1}{4},\frac{1}{4},0)$ and $(\frac{1}{4},-\frac{1}{4},0)$ to compute the Brillouin-zone averages. Including both k points in the calculation allows for breaking of the (010) reflection plane symmetry. Again, we checked this approximation by recomputing energy differences with four and nine k points in the *irreducible* Brillouin zone and the energy differences were converged to 4 meV/dimer. In order to compare properly, in terms of basis functions and k points, the total energies of the various symmetry reconstructions, we performed all calculations in a (4×2) unit cell and maintained either exact $b(2\times1)$, (4×1), $c(4\times2)$, or $p(2\times2)$ symmetry within this supercell. Therefore, our calculation uses a unit cell of 64 atoms and a volume equal to 112 atomic volumes.

To minimize the total energy of each symmetry reconstruction with respect to the atomic positions, we relaxed the atoms using an *ab initio* molecular-dynamics scheme[15,16] with quenching. This is a variational approach to minimizing the total energy of our system. The atomic coordinates and coefficients for the electric basis states are considered classical degrees of freedom whose equations of motion in phase space are given by a Lagrangian. The Lagrangian is formed with the kinetic-energy term taken to be the sum of the usual kinetic energy of the atoms plus a *fictitious* term $\frac{1}{2}m_e \; |\dot{\psi}|^2$ for the electrons. The energy functional for the system plays the role of the potential-energy term. When the system is completely quenched, the kinetic energy is zero and the equations of motion imply the potential-energy functional (the total-energy functional) is minimized with respect to the electronic and atomic degrees of freedom.

III. RESULTS

In Table I we list the total energy per dimer for the minimum energy $b(2\times1)$, $p(4\times1)$, $c(4\times2)$, and $p(2\times2)$ symmetry configurations, with the energy of the $b(2\times1)$ symmetry taken as the zero of energy. The 3-meV/dimer difference between the $p(2\times2)$ and $c(4\times2)$ symmetry reconstructions is within the uncertainties in the calculation. The result that the $p(2\times2)$ configuration is nearly degenerate with the $c(4\times2)$ configuration agrees with Kubby *et al.*[5] and Lambert *et al.*[8] Kubby *et al.*[5] studied the (100) surface using STM and observed both $p(2\times2)$ and $c(4\times2)$ coexisting with $b(2\times1)$ regions at room temperature. Lambert *et al.*,[8] using He diffraction, report $c(4\times2)$ symmetry with a residual $p(2\times2)$ component at $T<150$ K in agreement with Kevan,[10] who saw a LEED diffraction peak indicative of either $p(2\times2)$ or centered (2×2) at 220 K. However, this disagrees with the results of Culbertson, Yuk, and Feldman,[9] who report only $c(4\times2)$ diffraction patterns at low temperature.

We expected $p(2\times2)$ and $c(4\times2)$ to be close in energy because the previous tight-binding work of Ihm *et al.*[11] on Si and our previous *ab initio* work on Ge.[7] We determined that $c(4\times2)$ is lower in energy than $b(2\times1)$ because the alteration of up and down dimers along the dimer rows allows the second-layer atoms to relax. In order to keep bond distances close to the bulk value, the atoms in the second layer want to move towards the up dimmer atom to which they are bonded and away from the down dimer atom. This motion is energetically favorable only when the "up" and "down" dimers alternate along the dimer rows as in the $p(2\times2)$ and $c(4\times2)$ reconstructions. When the second-layer atoms are either bonded to two "up" or two "down" dimer atoms, they cannot move towards or away from a dimer without further stretching or compressing an already stretched or compressed bond, as the case may be. If this were the sole mechanism differentiating the energies of the various

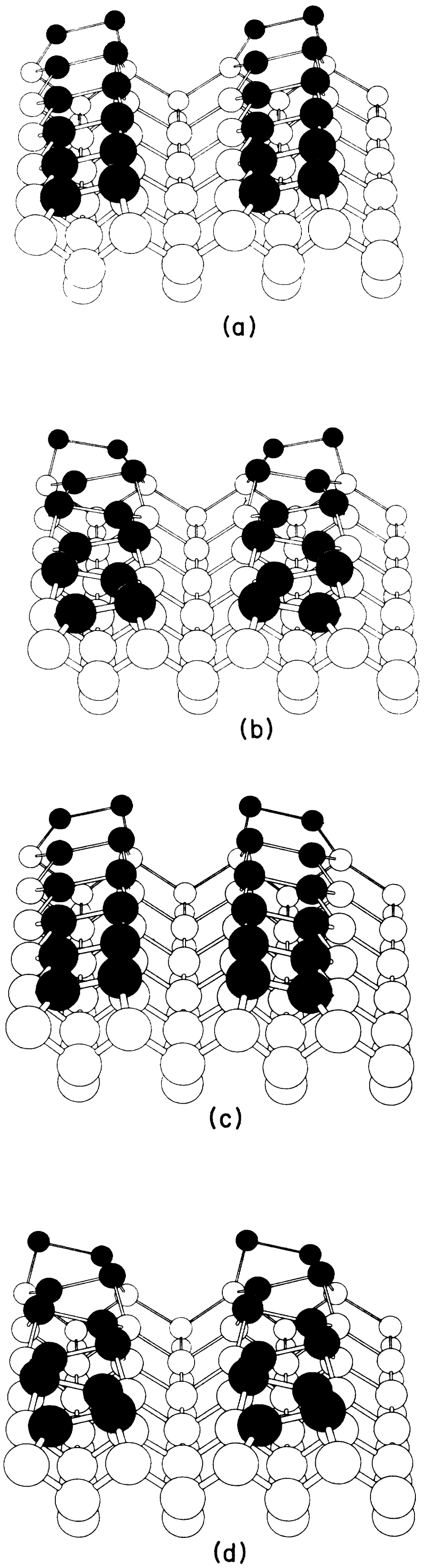

FIG. 1. Perspective view of dimer models of the Ge(100) surface. The solid atoms are the surface layer. (a) Buckled (2×1) symmetry configuration. (b) Centered (4×2) symmetry configuration. (c) Primitive (4×1) symmetry configuration. (d) Primitive (2×2) symmetry configuration.

TABLE I. Total energy of (2×1) family symmetry configurations.

System	Total energy (eV/dimer)
$b\ (2\times1)$	0.000
$p\ (4\times1)$	0.035
$c\ (4\times2)$	−0.066
$p\ (2\times2)$	−0.069

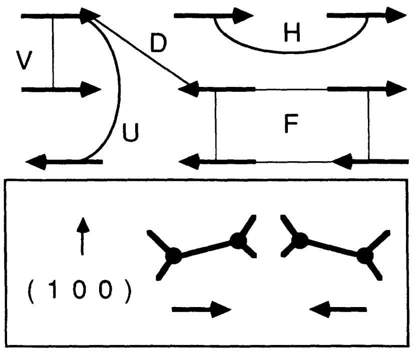

FIG. 2. Effective couplings between adjacent dimers.

dimer reconstructions, $p(2\times2)$ would be degenerate with $c(4\times2)$ and $p(4\times1)$ would be degenerate with $b(2\times1)$. Since $p(4\times1)$ is significantly higher in energy than $b(2\times1)$, this is strong evidence that an additional mechanism is at work.

The magnitudes of the displacements of the atoms are extremely similar between $p(2\times2)$ and $c(4\times2)$ dimers. In fact, if one takes the position of the two independent dimers in the $p(2\times2)$ geometry and maps them into the other two dimers according to $c(4\times2)$ rules, one gets an identical energy with the original minimum energy $c(4\times2)$. In contrast to previous work, there was negligible breaking of the reflection symmetry of the (010) plane. This symmetry breaking did not affect the total energy and probably arose from difficulties in performing those calculations. We find a dimer tilt of 14° for all four minimum-energy configurations.

IV. PHASE TRANSITION

To predict a phase-transition temperature one maps the dimer problem to a two-dimensional Ising-spin problem as did Ihm *et al.*[11] They considered the effective "spin" Hamiltonian

$$-H = v\sum_{i,j} s_{i,j}s_{i,j+1} + H\sum_{i} s_{i,j}s_{i+1,j}$$

$$+D\sum_{i,j} s_{i,j}s_{i+1,j+1} + U\sum_{i,j} s_{i,j}s_{i,j+2}$$

$$+F\sum_{i,j} s_{i,j}s_{i,j+1}s_{i+1,j}s_{i+1,j+1}$$

to describe the (2×1) family of dimers. This Hamiltonian includes all interactions up to two surface-atom spacings as shown in Fig. 2. The $T=0$ values of V, H, and D are derived from the total-energy differences of the four configurations and are given in Table II. As can be seen by the relative magnitude of V to H and D, the strongest coupling between dimers is along the rows. The terms involving U and F interactions contribute equally to the total energies for all four symmetries and are initially set equal to zero. A position-space renormalization-group–theory calculation is performed with a finite cluster of four cells of five sites each and the flows occur in the parameter space of V, H, D, and F. These values of the parameters lead to a phase-transition temperature of 380±100 K. This temperature is higher than the transition temperature measured by Kevan[10] and by Culbertson *et al.*[9] However, the phase transition is a weak second transition and we believe they measured the temperature at the onset of the transition. This conclusion agrees with the STM work of Kubby *et al.*,[5] who showed that domains of $b(2\times1)$ and $p(2\times2)$ coexist with $c(4\times2)$ at room temperature.

TABLE II. Effective coupling constants between adjacent dimers.

Coupling constant	E (meV)
V	-43
H	10
D	4

V. CONCLUSIONS

We have minimized the total energy of four different symmetry dimer reconstructions of the Ge(100) surface at $T=0$ K. To within the accuracy of the calculation, we find the $c(4\times2)$ and $p(2\times2)$ symmetry reconstructions are degenerate in energy. In contradiction to experiment, the $p(2\times2)$ reconstruction is slightly lower in energy. However, it is important to note that the theoretical results correspond to fixed surface strain. If the real system could alleviate strain by the formation of steps or other types of defects, this could change the relative energies of the $c(4\times2)$ and $p(2\times2)$ reconstructions. From this *ab initio* calculation we derive renormalization parameters for a simple two-dimensional Ising-spin model for the dimers and predict a phase-transition temperature of 380±100 K.

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