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Energetics of the Si(111) and Ge(111) surfaces and the effect of strain

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Using tight-binding models, the energies of a number of silicon and germanium (111) surfaces are studied. These include reconstructed surfaces with dimers and stacking faults (DS), simple adatom surfaces such as 2×2 and $c(2\times8)$, and more complicated cases with dimers, adatoms, and stacking faults (DAS). For reconstructed surfaces containing adatoms, it is found that a simple correction term dependent on the adatom concentration is needed in the present total-energy model to account for the unusual geometry. Similarities between the silicon and germanium reconstructions are seen and compare well with *ab initio* results. There are also some differences between silicon and germanium; for example, the DS surfaces are lower in energy than the relaxed (1×1) for silicon, but higher for germanium. Si(111) reconstructs into the DAS structure while Ge(111) goes to the simple adatom $c(2\times8)$ surface. The $c(2\times8)$, 7×7 DAS, (1×1), and 7×7 DS surface reconstructions of Ge(111) were studied with in-plane strain. For these surfaces, a strain of about 2% was sufficient to make the 7×7 DAS/DS surface lower in energy than the $c(2\times8)/(1\times1)$ surface. An analysis of the energy per atom showed that the dimer-row and associated first-layer atoms played a major part in the differing energy behavior, in agreement with an earlier proposal. An expansive strain was applied to the 2×2, 7×7 DAS, (1×1), and 7×7 DS surface reconstructions of Si(111). With a strain of about 2.5% the adatom surfaces switched relative energies, while the adatom free surfaces required only about 1.5% strain. As for germanium, the dimer-row and associated atoms were of major importance in the differing energy change.

I. INTRODUCTION

The elemental semiconductors, particularly silicon, have been the prototype for studies of surfaces. A wealth of information exists for the silicon surface as well as the germanium surface. This includes experimental results along with a number of theoretical treatments. To explain experimental findings, a reconstruction to a 2×1 periodic surface with large π bonded chains was proposed.[1] However, it was noticed that when annealed, the Si(111) surface became 7×7 and occasionally 5×5 or 9×9.[2–5] Takayanagi *et al.*[6] proposed that these new structures are one of a family of similar $(2n+1)\times(2n+1)$ dimer-adatom-stacking fault (DAS) reconstructions, the most important member for silicon being the 7×7 form. Germanium, which in many ways is so similar to silicon, forms a much different surface. The Ge(111) surface was proposed as an adatom covered $c(2\times8)$ arrangement based on the interpretation of experimental results.[5,7–9]

Many other reconstructions of these surfaces have also been studied theoretically, mostly the $(2)\times(2n)$ and some DAS.[10–13] Yet a number of reconstructions remain unstudied and many questions about the preferred reconstructions exist. In particular, under certain conditions, the Ge(111) surface is seen to undergo a transformation from the simple $c(2\times8)$ to a DAS form.[3,4,14–17] Tin overlayed on the germanium surface was seen to cause a reconstruction to a 7×7 or 5×5 DAS geometry.[14,15] A similar behavior was seen for germanium grown on Si(111) and by the alloying both in the growth and after growth (by heating) of germanium and silicon.[3,4,16,17] Important among these works are two which indicate that compression alone is sufficient to induce the transformation of the Ge surface.[16,17] The silicon surface has also been seen to undergo transformations from a 7×7 DAS surface to a 5×5 DAS surface.[3,4,16] Transformations to a 1×1 arrangement have also, possibly, been seen.[4,14]

These transformations are, according to one model,[11,18,19] brought about primarily because of the dimer rows in the DAS geometries. In this dimer-row model, developed for silicon, the adatoms do not play an important role in determining the overall geometry. By looking at surface stresses the model predicted the adatom-free silicon transformation. Some estimates of surface stress were obtained from classical force fields since tight-binding or *ab initio* results are not available. However, adatoms may not be negligible in some cases. In fact, tin has been seen to cause the 7×7 DAS surface on germanium and has been associated with the adatoms.[14,15]

Previously, we developed tight-binding models for silicon and germanium.[20] These models focused on the strain dependence of the tight-binding parameters for the tetrahedral structure. By fitting the tight-binding interaction parameters to *ab initio* band structure at fourteen volumes ranging from 75% to 190% of the ideal volume, the distance dependence for the parameters was found. These were then used on a number of other structures, including the higher coordinated crystals and Si_2. By comparing with *ab initio* total-energy values for a number of structures, a repulsive potential was itself parametrized. This repulsive potential consisted of a structure-dependent term multiplied by a pairwise potential. A number of test cases were performed including Si_3, Ge_2, Ge_3, phonons, vacancies, interstitials, and other crystals, all showing very good results with *ab ini-*

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tio values.[20]

This paper focuses on the reconstructions of various silicon and germanium (111) surfaces. For surface reconstructions, the adatoms are shown to be primarily important only to lowering energies. The geometry that is lowest in energy without adatoms (compared to other adatom-free surfaces) is usually lowest with adatoms (compared to other adatom surfaces). The adatoms do not seem important, therefore, in determing the surface geometry except in certain instances. This work also shows why for silicon 7×7 DAS rather than $c(2\times8)$ is most often seen and for germanium, $c(2\times8)$ rather than 7×7 DAS. In addition, why Ge(111) more readily forms the 7×7 DAS surface than silicon forms the $c(2\times8)$ surface will be discussed. The importance of a variety of surface atoms to the determination of surface stress and energy will also be shown. Particularly, this will center on the adatoms, first-layer atoms, and dimer-row atoms. Section II covers adatom and adatom-free reconstructions of both silicon and germanium. Many of these surfaces, particularly for silicon, represent test cases and show quite good agreement with *ab initio* results. In particular, the energy separations, atomic coordinates, and charge densities were all quite good for the simple surfaces. A number of reconstructions, however, have not been previously treated with tight-binding or *ab initio* techniques; among these are the silicon $c(2\times8)$ and 7×7 dimer-stacking-fault (DS) surfaces and the germanium 5×5, 7×7, and 9×9 DAS and DS surfaces. Section III treats the transformation of the germanium (111) surface under compressive stress. Four germanium surfaces, the adatom surfaces $c(2\times8)$ and 7×7 DAS and the adatom-free surfaces (1×1) and 7×7 DS are compressed from the germanium lattice constant to the silicon lattice constant. Finally, in Sec. IV, a study of the silicon (111) surface under expansive stress is discussed. This transformation has been treated via the dimer-row model,[11,18,19] but is discussed here using a uniform treatment of the 2×2, 7×7 DAS, 1×1, and 7×7 DS surfaces.

II. UNSTRAINED Si(111) AND Ge(111)

A. Calculational details

Of the theoretical techniques available, classical potentials can be ruled out because of poor results for the (111) surfaces of silicon.[21] The size of the systems in question particularly those in Secs. III and IV prevent the ready use of *ab initio* methods. Therefore, the best possible treatment would be a tight-binding analysis. The formalism for the binding energy is the same as that presented elsewhere with a simplification to a cutoff function.[20] (This simplification is discussed below.)

All calculations for silicon were performed with the experimental lattice constant 5.43 Å.[22] The theoretical lattice constant for germanium (5.655 Å) was used.[23] The simple (111) and (100) unrelaxed surfaces were calculated using unit cells consisting of five bilayers. For the remaining surfaces with different periodicities, larger cells were needed. To agree with the cell sizes from similar calculations,[12,24] the large cells consisted of four silicon or six germanium layers (not including any adatom layer) with a layer of hydrogen atoms bonded to the lowest layer. As an example, the 5×5 DAS surface has a 5×5 cell with one adatom layer and four additional silicon layers and one hydrogen layer to make a total of 125 atoms. The total number of atoms for the germanium 7×7 DAS seven layer calculation was 347. As a reference, the unrelaxed (111) surface was recalculated in a similar setup.

The use of one k point Γ for supercells having about 25 or more (1×1) surface cells is common and was continued here.[12,25,26] More k points were needed for smaller cells. It is equivalent to using one k point (Γ) with a larger nonprimitive surface cell. The k points were chosen such that, for silicon, the $\sqrt{3}\times\sqrt{3}$ and 2×2 surfaces had an effective 6×6 cell; the $c(2\times4)$, $c(2\times8)$, π-bonded, unrelaxed and relaxed (111) for Si and Ge, and 2×2 for Ge had effectively 6×8 cells. The (111) faulted cell used a 7×7 cell for no reason other than it is the same size as the 7×7 DAS cell. In addition, the 5×5 surfaces were also studied in a 10×10 supercell to examine size effects for these calculations. Typically, the number of atoms in an effective cell was about 200 for most silicon calculations and about 340 for most germanium calculations. Symmetry was imposed on every structure.

The hydrogen which served as the bottom layer of each cell was included to tie off the dangling bonds present at the bottom of the cell. The values for the silicon-hydrogen interaction parameters are 1.50, 3.68, and 2.05 eV for $ss\sigma$, $sp\sigma$, and s_0, respectively. The hydrogen-germanium values are 1.75, 3.86, and 2.85 eV for $ss\sigma$, $sp\sigma$, and s_0, respectively. The values were adjusted to maintain a bulklike charge distribution on the bottom. Since differences between surface geometries and cell sizes did not seriously affect these electron densities, the interaction parameters were kept constant for all cells.

Forces for relaxation were calculated by taking the derivative of the repulsive potential and by using Hellmann-Feynman forces for the tight-binding part.[27–29] The forces were then minimized until no lower-energy structure could be found; this often resulted in the forces being at or close to zero (less than 0.1 eV/Å). Although the surfaces can at times show quite large relaxations, typically the bond lengths between first nearest neighbors are not much different from the bulk bond length. This is not to say that all the changes in bond length were small, but few bonds approached a very compact nature. Because of this more open structure, the cutoff function Γ' that was developed in the tight-binding models[20] seemed to be relatively unnecessary and a constant cutoff was imposed instead. The constant cutoff was set at 3.0 Å. Use of the constant cutoff facilitated the calculation of the derivatives necessary for the force calculations and simplified the energy calculations.

B. Silicon surfaces

Table I shows the results for the (100) and the (111) surfaces for both silicon and germanium. The tight-binding surface energies for silicon (111) and (100) are lower than the *ab initio* values. One possible reason for

TABLE I. Silicon and germanium unreconstructed surface energies as compared to *ab initio* and bond counting energies. The energy is in eV per surface atom.

	Present	*ab initio*	Bond counting
Silicon			
Si(100)	1.97	2.5[a]	2.3
Si(111)	1.1	1.6[b]	1.2
Germanium			
Ge(100)	1.57		1.9
Ge(111)	0.98	1.22,[c] >1.40[d]	0.95

[a] Reference 30.

[b] Reference 39.

[c] Reference 13.

[d] Reference 10.

this lower value could be due to the imperfect modeling of the repulsive bond energy in the diamond to trimer region, indicating that the repulsive term is too weak for the surface. This could be fixed by strengthening the first term in the coordination-dependent function ω,[20] but leaving the over all bulk values alone. It was also noted that the palne-wave energy cutoffs used for the *ab initio* calculations were very low. For Si(100), it was stated that the cutoff was 4.3 Ry,[30] while another source indicated that the energy of the (100) surface was still converging beyond 6.5 Ry.[31] This continued convergence might lead to a drop of at least another approximately 0.24 eV/atom,[32] bringing the present work and *ab initio* values closer together.

Bond counting energies which are determined from the number of bonds broken are also listed in Table I. These energies were found by using experimental cohesive energies.[23] For the (111) surface these show much better agreement while only some improvement is made for the (100) surface.

It is also possible that the error could arise from the electronic contribution. This was difficult to gauge. The band structures for the 2×2 and $\sqrt{3}\times\sqrt{3}$ surfaces were calculated and although they were not perfect it seemed quite unlikely that the error for the (100) and (111) unrelaxed surfaces could come from this alone.

The calculated relative values for various Si(111) surfaces are listed in Table II along with the *ab initio* results for comparison. Among the *ab initio* values, there was agreement in ordering and in some cases energy for the results of different groups work. However, the values were at times far from consistent. One reason for the differences is due to the plane-wave cutoff used. Certain structures such as the adatom surfaces have been shown to reach well-converged results only at higher-energy cutoffs than would be necessary for other surfaces.[10] For reference the plane-wave cutoffs are in parentheses after the corresponding *ab initio* value. The exchange correlation term as well as the pseudopotential provide additional reasons for the differences.

The energy difference, listed in Table II, for the faulted and unfaulted relaxed surface were found to be 80 meV, which is in reasonable agreement with the *ab initio* value of approximately 60 meV.[10] The first layer of the faulted surface is about 0.07 Å above that of the unfaulted surface and the second layers were at nearly the same levels. The direction of the relaxation is correct, but the movement of the atoms is about half of the *ab initio* results.[10]

The silicon π-bonded surface energy was quite well modeled being about 0.35 eV lower in energy than the unrelaxed (1×1) surface again listed in Table II. *Ab initio* and earlier tight-binding results give this separation to be 0.36 eV.[33,34] Some movement relative to Pandey's values was noticed.[1] In addition, a small buckling developed in

TABLE II. Comparison of tight-binding silicon (111) surface energies (eV) per 1×1 unit to *ab initio* results. $/r$, $/\pi$, and $/(7\times7)$ mean relative to the relaxed surface, the π-bonded chain surface, and the 7×7 DAS surface, respectively. *Ab initio* calculation cutoffs (in Ry) are in parentheses.

	Present		*ab initio*
	uncorrected	corrected	
Adatom-free surfaces			
unrelaxed	0.0		
relaxed	-0.031		-0.17,[a] -0.15 (6)[b]
faulted (111)	0.048		$\approx$0.06$/r$ (8)[c]
π	-0.353		-0.36 (6),[d] -0.30$/r$ (8)[e]
DS(5×5)	-0.063		
DS(7×7)	-0.048		
Adatom surfaces			
$\sqrt{3}\times\sqrt{3}$	0.207	-0.24$/r$	-0.28 (6),[f] -0.21$/r$ (12)[c]
2×2 T_4	0.067	-0.31$/r$	-0.27$/r$ (12)[c]
$c(2\times8)$	0.058	-0.32$/r$	
DAS(5×5)	0.012	0.01$/(7\times7)$	0.015$/(7\times7)$ (7)[g]
DAS(7×7)	0.007	-0.05$/\pi$	-0.06$/\pi$ (8)[h]

[a] Reference 40.

[b] Reference 41.

[c] Reference 10.

[d] Reference 33.

[e] Reference 11.

[f] Reference 42.

[g] Reference 25.

[h] Reference 26.

the surface atoms with the trend being similar although smaller in nature to that shown by *ab initio* work.[35]

The adatom free surfaces 7×7 DS and 5×5 DS were both lower in energy than the 1×1 relaxed surface. Since the DS surface consists of 1×1 regions and dimer rows, the fact that the two DS surfaces are lower in energy indicates the importance of the dimer rows. It is also important to notice that the 5×5 DS surface is lower in energy than the 7×7 DS surface while the 5×5 DAS surface is slightly higher in energy than the 7×7 DAS surface. Since the adatoms are the only difference, this indicates the influence that adatoms can have on the surface energy for the DAS models. For the 5×5 DAS surface, the use of a 10×10 effective cell (with one k point Γ) lowers the energy by 13 meV per 1×1 unit. It is the lower value that is listed in Table II.

All of the adatom covered surfaces came out to be too high in energy. This turned out to be due, at least in part, to the modeling of the adatom energies both by the repulsive potential and the band energy E_{bs}. This was evident when the 2×2 T_4 configuration was made a 2×2 T_3 surface. By preventing the T_4 configuration from forming the adatom to second-layer atom bond, the energy for the surface dropped considerably. The fact that this bond was unfavorable suggests that d orbital modeling may be needed for this interaction and that the repulsive potential may be relatively too strong compared with the ideal surface.

By looking at the separation of the 7×7 DAS, $c(2\times8)$, and 2×2 energies, it is seen that they agreed fairly well with the *ab initio* values. The difference in the 5×5 DAS and 7×7 DAS energies was in reasonable agreement with *ab initio* work. These two surfaces and the 2×2 and $c(2\times8)$ surfaces have adatom concentrations of about 0.25 per (1×1) cell. The adatom concentration suggests that a simple adatom correction could take care of most of the energy discrepancies of the adatom surfaces.

To correct the energies of the surfaces, a simple formula was used to determine the additional lowering in energy due to adatoms. If the energy of the surface per 1×1 cell is E_{sur}, then

$$E_{\mathrm{sur}} = E_{\mathrm{unc,sur}} + \alpha\eta_a^{\beta} \; . \tag{1}$$

$E_{\mathrm{unc,sur}}$ is the uncorrected energy per 1×1 cell of the surface and α is a constant. η_a is the adatom density per 1×1 cell. This is then raised to the β power. β was not assumed to be one since a number of factors might affect it. For example, the adatoms tend to transfer charge from their dangling bonds to first-layer atoms, which also have dangling bonds. As the concentration of adatoms increases, the amount of charge transferred and the number of first-layer atoms with dangling bonds and adatoms are changing. The tight-binding models are already predicting this behavior, but for the adatoms the prediction may not be complete requiring a correction term that does not give β equal to one.

The corrected values are tabulated in Table II. For the silicon calculations with an emphasis on the 7×7 DAS, α was -0.82 eV and β was $\frac{1}{2}$. The value for β may be valid only for the range of adatom coverages considered and is used for the model to predict some of the adatom energy correctly. It is possible that changes to the model might affect β. The corrected values show a good fit to the *ab initio* values. Compared to the *ab initio* separation of 60 meV, 2×2 and $\sqrt{3}\times\sqrt{3}$ are now about 70 meV apart.[10] The 7×7 DAS surface is about 50 meV below the π surface which compares well with the *ab initio* value of 60 meV.[26] The separation of the 7×7 DAS and the 5×5 DAS became 10 meV, in good agreement with the *ab initio* value of 15 meV.[25]

Regarding the atomic coordinates, in agreement with *ab initio* work the first-layer atoms of the 2×2 and $\sqrt{3}\times\sqrt{3}$ T_4 surfaces bonded to the adatoms were seen to be drawn to the adatom. The projected bond distance on the Si(111) plane gave 2.09 Å for the 2×2 surface, in good agreement with the *ab initio* value of 2.11 Å (Ref. 10) and 2.12 Å for the $\sqrt{3}\times\sqrt{3}$ surface, which is somewhat larger than the *ab initio* value of 2.07 Å. A comparison of the electronic band structures for the 2×2 surface showed that there was a gap, in agreement with *ab initio* calculations,[10] although it tended to close up at Γ. Also the highest occupied (S_2) and the lowest unoccupied (S_1) surface bands were not as flat as shown in *ab initio* calculations. The charge distribution for the S_1 and S_2 bands were very much like those of the *ab initio* work. The S_1 charge density centered on the adatom and the third-layer atom below the adatom. For S_2, the rest atom picked up most of the charge density, with the third-layer atoms associated with rest atoms being slightly larger.

The $c(2\times8)$ surface showed asymmetries which were most pronounced among the adatoms and the first-layer atoms particularly the rest atoms. The adatom asymmetries fell roughly into two groups that could be separated into 2×2 and $c(2\times4)$ subunits. These results closely paralleled the behavior for the adatoms and first-layer atoms that were seen in the *ab initio* calculation for Ge(111) $c(2\times8)$.[24] The atomic coordinates neglecting the asymmetries in the first layer for Si(111) $c(2\times8)$ were similar to those seen in the 2×2 surface.

Results for the DAS structure are very similar to those of previous tight-binding[12] and *ab initio* calculations.[26] The first and second layers showed a general movement away from the bulk, which agreed with the *ab initio* calculation. The adatoms showed a very small movement toward the bulk; *ab initio* values showed a small (0.03 Å) adatom movement away from the bulk.

A comparison was made of the atomic positions in the 7×7 DAS surface and the 7×7 DS surface. The general difference between these surfaces was a large rest atom (in DAS) change and a large change in the planar locations of the first-layer atoms bonded to adatoms. Corresponding changes occurred for atoms related to these atoms, in particular the second- and third-layer atoms associated with adatoms. By the second layer most atoms were within about 0.03 Å of their ideal positions in the DS cell. Very few changes were seen from the 5×5 DAS model to the 7×7 DAS model in terms of distances away from the bulk. The charge transfers noticed in *ab initio* work for the 7×7 DAS surface[25] were to a certain extent repeated in the current case, in that the adatoms on the unfaulted side transferred more charge than the faulted side adatoms did. However, the center adatoms transferred slightly more charge than the corner adatoms and in the 5×5 structure very little difference was seen between the two sides.

C. Germanium surfaces

In Table I, the surface energies for unrelaxed (111) and (001) germanium are presented with *ab initio* and bond counting values for comparison. As compared to the bond counting values the (111) surface is in good agreement while the (100) surface is noticeably low. For the (111) surface, the value was lower than the *ab initio* result. Many of the arguments used for silicon to explain the low values can be used here—mainly that the repulsive potential was possibly too weak in the diamond to trimer range (which would cover these two surfaces) and possibly that the E_{bs} is in error.

The energies for a number of (111) surfaces can be found in Table III. The (111) surface showed relaxation similar to the silicon (111) surface. The first layer relative to the second dropped approximately 0.08 Å, which is similar to the 0.14 Å given for the first layer of silicon.[10] With the possible exception of the second layer, the faulted to unfaulted comparison again agreed with *ab initio* work for silicon.[10] The energy separation of 60 meV was close to the *ab initio* value of 50 meV.[10]

The result for the energy of the π surface is somewhat poor. Relative to the other interaction parameters, $pp\pi$ has a much lower value for germanium than it does in silicon.[20] This might be the reason for the high energy. The reason for the smaller relative value could be due to changes in the needed behavior of the parameters to accurately model the germanium bulk system. If this were the case, additional parameters such as more distant neighbors or more orbitals for the first nearest neighbor would probably be sufficient to correct the error. In agreement with results for silicon both with the present work and *ab initio* calculations,[35] there was a small amount of buckling present.

Unlike silicon where there was a distinct difference between 2×2 and $c(2\times8)$, here 2×2, $c(2\times4)$, and $c(2\times8)$ are virtually indistinguishable by energy. However, *ab initio* work has found the $c(2\times4)$ surface to be 60 meV above $c(2\times8)$.[24] It is possible that for silicon the use of a 6×6 surface cell for 2×2 and 6×8 for $c(2\times8)$ artificially created an energy difference and that given a larger cell there would be practically no difference. This would suggest that these potentials are incapable of modeling the interactions that would be necessary to distinguish structures so similar as the 2×2, $c(2\times4)$, and $c(2\times8)$.

The 7×7 DAS surface was found to be above the $c(2\times8)$ surface just as the 7×7 DS surface was higher than the (111) relaxed surface. This was similar to the situation for silicon where the 7×7 DS surface was lower than the (111) relaxed surface and the 7×7 DAS surface being lower in energy than the $c(2\times8)$ surface. By using the relaxed positions from 7×7 DS and DAS to form the 5×5 DS and DAS surfaces, it was found that these were higher in energy than the 7×7 forms. The 5×5 structures were allowed to further relax from the 7×7 derived structure. This resulted in only a 6-meV drop occurring for 5×5 DAS while the DS surface energy dropped 20 meV. Relying on the fact that only small relaxations were seen

TABLE III. Comparison of germanium (111) surface energies (eV) per 1×1 unit to *ab initio* results. /*r* means relative to the relaxed surface. *Ab initio* calculation cutoffs (in Ry) are in parentheses.

	Present		*ab initio*
	uncorrected	corrected	
Adatom free surfaces			
unrelaxed	0.0		
relaxed	-0.019		
faulted (111)	0.040		≈0.05/r (8)[a]
π	-0.108		-0.28,[b] -0.32 (5),[c] -0.34 (8)[d]
DS(5×5)	0.055		
DS(7×7)	0.017		
DS(9×9)	0.011		
Adatom surfaces			
2×2	0.091	-0.31/*r*	-0.2/*r* (12)[a]
$c(2\times4)$	0.090		-0.27[b]
$c(2\times8)$	0.089	-0.33	-0.33[b]
DAS(5×5)	0.143	-0.268	
DAS(7×7)	0.107	-0.308	
DAS(9×9)	0.104	-0.312	

[a] Reference 10.
[b] Reference 24.
[c] Reference 43.
[d] Reference 44.

for 5×5, the relaxed 7×7 surfaces were used to derive 9×9 surfaces. No further relaxations were allowed on the 9×9 because of the size of the cells (up to 577 atoms). These turned out to be nearly equivalent in energy with the 7×7 surfaces.

In order to evaluate the 5×5 in better relation to the 7×7 and 9×9 surfaces and to test the effect of using one k point, the relaxed 5×5 cells were calculated with four points in the Brillouin zone which are equivalent to the Γ point in a 10×10 cell consisting of four 5×5 cells. A noticeable drop (45 meV per 1×1 cell) occurred, but still the 5×5 surfaces were the highest of the DAS and DS surfaces. This lower energy is shown in Table III. It is also important to note that the 5×5 surface was much higher relative to the 7×7 DAS surface in germanium than it was for silicon. This is suggestive of the reason why the two have different minimum-energy structures since it appears that for germanium a switch to a smaller DAS surface and therefore more dimer row atoms per unit cell is less favorable. This topic will be dealt with in detail in the next section.

The germanium results agree well with experimental evidence, although again an adatom shift must be included so that the adatom-surfaces are below the adatom-free surfaces. To correct the energies of the germanium surfaces, the simple adatom correction formula in Eq. (1) is used again. The corrected values are tabulated in Table III. For the germanium calculations with an emphasis on $c(2\times8)$, α was -0.838 eV and β was again $\frac{1}{2}$. The present model for germanium, therefore, is also able to predict some of the adatom dependence, although not all of it. The corrected values show a good ordering relative to experimental evidence. Obviously, no change was made in the minute difference between 2×2, $c(2\times4)$, and $c(2\times8)$. The separation of the 7×7 DAS and the 5×5 DAS became 40 meV, indicating that for germanium the 5×5 surface is much higher relative to the 7×7 surface than it was in silicon. 7×7 DAS was above 9×9 DAS by 4 meV, but this value is still well within the error limits for the calculations.

The atomic arrangement for the 2×2 T_4 surface agreed well with the scaled (by lattice constants) values from silicon *ab initio* calculations.[10] The adatoms have moved away from the bulk compared to the silicon results. Further layers follow the silicon results (both *ab initio* and present work), but are typically lower by a small amount. The more mobile atoms are those associated with the adatoms, the second-layer atom below it and the third below that. Very little movement is seen for the fourth and fifth layers. The first-layer atoms attached to the adatoms draw closer and have a projected bond length of 2.20 Å. The second layer to adatom bond length is 2.81 Å compared to the adatom to first-layer bond length of 2.66 Å.

For $c(2\times4)$ the atomic coordinates were very similar to the 2×2 results. Adatom heights showed a slight difference with one adatom per $c(2\times4)$ lower than the other. The accompanying rest atoms also showed a small difference. The adatom to first-layer projected bond distance was 2.19 Å for the lower adatom and 2.18 Å for the higher adatom; most other atoms were identical to the 2×2 surface except for the slight changes due to the two different adatoms and rest atoms in each cell.

For $c(2\times8)$ the adatom splitting was barely noticeable, but the rest atom splitting increased significantly to a difference of about 0.02 Å. This agreed with *ab initio* work[24] where the adatom buckling was less than 0.002 Å and the rest atom buckling was 0.03 Å. As usual these differences were carried down into the lower layers with diminishing effect. There was less of a difference in the adatoms to first-layer projected bond length for this surface with the length being nearly equal at about 2.19 Å. Both the rest atoms and the adatoms were about 0.10 Å lower than the equivalent *ab initio* values.[24] The coordinates from the *ab initio* calculation of $c(2\times8)$ (Ref. 24) were relaxed and found to be slightly higher in energy than the $c(2\times8)$ found here. The *ab initio* coordinates showed a much larger symmetry breaking in some regions and the tight-binding model is probably unable to find any energy advantage to this.

The charge transfer for the 7×7 surface was similar to that for the silicon cell. The central adatoms transferred more charge than the outer adatoms. This charge was transferred to the rest atoms, the second-layer atoms beneath the adatoms, and the dimer atoms near the corner holes.

A comparison of the Ge 7×7 DAS to a scaled version of the silicon 7×7 DAS showed that the Ge adatoms preferred positions much further away from the bulk, as did the dimer atoms, the rest atoms, and the corner atom. The only atoms to move down compared to silicon were the second-layer atom under the adatoms. There were no significant movements in the plane. The Ge 7×7 DAS at a planar lattice length of silicon was compared to the silicon 7×7 DAS (Ref. 36) and showed that the adatoms, first, dimer, and corner atoms were higher. The only significant planar movements showed that for germanium the dimers and the third-layer atoms associated with them had moved further apart than they were in silicon.

III. STRAINED Ge(111)

Two experimental works show that compression is sufficient to drive a transformation of the germanium $c(2\times8)$ surface to a 7×7 DAS reconstruction.[16,17] In both works germanium was overlayed on silicon, one using only a few overlayers[16] and the other using a much greater thickness.[17] The silicon substrate with a lattice length about 4% smaller than germanium's served to compress the germanium surface. Each work found that germanium forms a 7×7 DAS structure and in one that it maintained this structure even for overlayers up to 1000 Å thick. The possibility that the germanium surface was conforming to the silicon 7×7 DAS template was refuted due to the fact that the bulk of the germanium film in the large overlayer was only hexagonally distorted and did not show 7×7 periodicity.[17]

The question remains though as to why the germanium surface undergoes this change. Because the surface transforms under compression, it is reasonable to assume that some strain-dependent mechanism is determining the change. Which part of the surface is most active in the transition is not fully known. One attempt to explain the transformation centers on the dimer rows present on the 7×7 DAS and DS surfaces.[11,18,19] In the model, the effect of adatoms is believed to be rather small. When the dimer rows form they are able to reduce the number of dangling bonds present on the surface which should decrease the surface energy. The model states that this energy reduction may be sufficient to overcome the increase in energy associated with the dimer rows being under tensile stress.[11] For germanium, the reduction in energy by reducing dangling bonds is insufficient, according to the model, and normally a DS or DAS surface will not develop. Under compression, the adatom-free germanium surface should transform from a 1×1 geometry to the 7×7 DS surface. The compression relieves the tensile stress until it is favorable for the dimer rows to form. With the addition of adatoms these surfaces would go from 1×1 to $c(2\times8)$ and 7×7 DS to 7×7 DAS.

A. Calculational details

The procedure used here was the same as the one used for the other silicon and germanium surface calculations. In order to determine the formation energy for a compressed (expanded) (C/E) surface relative to a similarly C/E bulk, the energy of the C/E bulk was needed. In order to do this, a bulk cell was C/E in the two dimensions parallel to the (111) surface. The perpendicular lattice constant was then varied to minimize the bulk energy. This produced the two-dimensional C/E bulk energy values listed in Table IV.

The first column of Table IV lists the cubic lattice constant in the plane of compression (expansion). The second column list the lattice constant perpendicular to the (111) surface. Typically, a bulk compressed in two dimensions would lower its energy some by expanding in the third dimension (perpendicular to the surface). As can be seen the 5.43-Å values for silicon and 5.655-Å values for germanium have the lowest bulk energies. Since all other bulk values are higher, it is possible that some surfaces (with larger or smaller in-plane lattice constants) will show a lower energy of formation from their particular bulk.

TABLE IV. Silicon and germanium bulk energies under compression and expansion.

Lattice constant (Å) In plane	 Vertical	Energy (eV/atom)
	Silicon	
5.35	5.430	-4.9110
5.43	5.430	-4.9126
5.50	5.376	-4.9054
5.55	5.349	-4.8958
5.65	5.294	-4.8653
	Germanium	
5.43	5.909	-4.0276
5.55	5.768	-4.0428
5.60	5.712	-4.0460
5.655	5.655	-4.0470
5.75	5.570	-4.0449

To saturate the dangling bonds on the bottom of the cells hydrogen atoms were again added and the parameters given in Sec. II were again used. Because the hydrogen-germanium and hydrogen-silicon tight-binding interaction had no known distance dependence, the distance was not varied as the cells underwent scale changes. This produced a uniform energy contribution from the Si-H and Ge-H interactions to each super cell and each 1×1 cell since there is one hydrogen-semiconductor interaction per 1×1 cell. The values for the Si-H and Ge-H interactions were initially set to mimic a Si-Si or Ge-Ge charge interaction by holding the charge at four electrons per semiconductor and one per hydrogen. During the expansion and compression these electron densities changed very little (≤ 0.04) so the parameters did not need to be changed to prevent large charge flow.

B. Results

For the compression of the Ge(111) surface, six surfaces were considered, 7×7 DS, relaxed 1×1, 7×7 DAS, $c(2\times8)$, 2×2, and $c(2\times4)$. Since the energies for the $c(2\times8)$, $c(2\times4)$, and 2×2 surfaces were virtually identical, only the $c(2\times8)$ energies will be discussed. This similarity indicated that the present model has difficulty with the long-range differences between these three surfaces. For germanium, the adatom surfaces were left uncorrected; the effect of the correction although small will be discussed later.

The surface energy results (relative to the bulk with corresponding in-plane lattice constants) for $c(2\times8)$ and 7×7 DAS are shown in Fig. 1(a). It can be seen that for $c(2\times8)$ the lowest energy of formation was the ideal lattice constant. 7×7 DAS had its lowest energy at around 5.6 Å. As the compression increased the 7×7 DAS surface did not rise as fast as the $c(2\times8)$ surface and the two eventually switched order at about 5.56 Å. Under expansion, $c(2\times8)$ remained below 7×7 DAS and for the regions considered rose at a slower pace.

With the adatom correction discussed in Sec. II, the energies of both surfaces would drop almost equally. A slight difference would occur since the $c(2\times8)$ surface has 0.25 adatoms per 1×1 cell and the 7×7 DAS surface has $\frac{12}{49}$ adatoms per 1×1 cell. This would result in a change in the location at which the two surfaces switch and the new transformation point would be about 5.53 Å. With or without the adatom correction energy the results are not far from the experimental value of ≈5.63 Å,[17] although the compression is slightly larger.

The results for the adatom free surfaces are shown in Fig. 1(b). As can be seen they behave much like the adatom surfaces. It is evident that a difference in stress for the two surfaces leads to the transformation. By looking at the differences between (a) and (b) in Fig. 1 it can be seen that the adatoms do make some difference. Most noticeable is the reduction in the separation between the 1×1 and 7×7 DS surfaces upon addition of adatoms which leads to the lower compression necessary to cause the transformation. Another is the change in slope between the adatom and adatom free surfaces. This slope can be related to the surface stress σ by[19]

$$\frac{dE}{d\epsilon} = A\,\mathrm{Tr}(\sigma) \tag{2}$$

where A is the surface area, E is the total surface energy, and ϵ is the isotropic strain. The stress is usually reported as σ_{ii}, which can be found from

$$\sigma_{ii} = \frac{1}{2}\,\mathrm{Tr}(\sigma). \tag{3}$$

Using these formulas the surface stress for the relaxed (1×1) surface was found to be −0.25 eV per 1×1, which is in poor agreement with the *ab initio* value of −0.73 eV/(1×1).[10] A similar calculation found the stress for the 2×2 surface to be about 0.52 eV/(1×1). This can be compared to the much larger value of 1.43 eV/(1×1) from *ab initio* work.[10] The surface stress with the present model for the $c(2\times8)$ surface is the same and it could be assumed that the $c(2\times8)$ energy curve in Fig. 1 should show a more positive slope around 5.655 Å. The stress for the 7×7 DS surface was 0.45 eV/(1×1) and for the 7×7 DAS it was 0.59 eV/(1×1). Since the triangular islands of the DAS surface are also 2×2 a change to the DAS energy slope is probably also necessary. Such a change would probably nearly cancel out the change made to the $c(2\times8)$ energy curve resulting in little difference from the present results. Overall the stresses are of the correct sign, but too small in magnitude. The error could be attributed to a number of factors concerning the formalism of the models used; however, the results are reasonable compared to some classical models[11] and show the effect of the adatoms and different surface geometries.

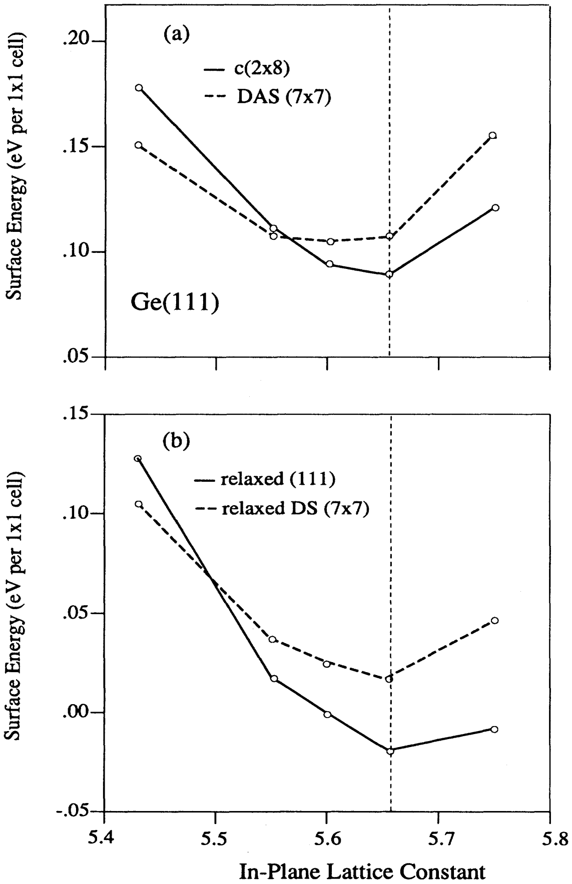

FIG. 1. (a) Surface energy per (1×1) for two strained germanium (111) adatoms surfaces. The ideal lattice constant is a vertical, dotted line. (b) Surface energy per (1×1) for the two germanium surfaces in (a) without adatoms. The lattice constant is in angstroms.

C. Analysis

Although the adatom-free results agree with the dimer-row model, it would be beneficial to analyze the change in each atom's energy. It was therefore necessary to find the band energy E_{bs} and repulsive energy E_{rep} per individual atom. For the electronic part, this was determined by multiplying each occupied eigenvalue by its weight at each atom and then summing over all occupied eigenvalues. Written explicitly,

$$(E_{bs})_i = \sum_j f_j \epsilon_j \rho_i(\epsilon_j) \tag{4}$$

where ϵ_j is the energy of the level j, $\rho_i(\epsilon_j)$ is the charge on a particular atom i for that energy level, and f_j equals 1 (occupied) or 0 (unoccupied). Combined with the repulsive energy per atom the total energy per atom can be found. It would be best to compare the changes in energy of one surface relative to another. To find the relative energies, the change in energy per atom for each layer of the relaxed (1×1) surface between 5.655 Å and 5.43 Å was found. This was then used as a reference (per atom in each layer) for changes in energy of the DS model. By relating the DS energy to the relaxed (1×1) it would be possible to see which atoms caused a rise or drop in energy relative to the relaxed (1×1) surface. These energy changes are shown in Fig. 2 for the compression from 5.655 Å to 5.43 Å. The energy term is separated into positive and negative figures. Those atoms which show the most change are black (normally larger than 0.25 eV) while those showing the least are white. The hatched patterns represent in between changes. It is possible that a white atom showed some change, but that it was just insufficient to appear here.

Figure 2(a) shows the areas that tend to increase the relative energy of the DS surface over the relaxed (1×1) surface. These areas are predominately the central regions of each island and the energy increase was seen to come mainly from the band energy. Although these regions did move towards the vacuum some, they were not very mobile in any other sense. The unfaulted side had additional movement of the second-layer atoms associated with the interior. This movement and faulting may be the cause of the difference seen between the two halves. It seems possible that by being in the interior these regions were less able to take advantage of the effects of the dimer rows and corner hole. The second-layer atoms that also show a rise in energy showed a movement down into the bulk as the cell was compressed. This is very likely caused by the effect of the corner hole, which tends to pin down the first-layer atoms nearest it.

The atoms associated with the overall energy decrease that gave the compressed DS surface to be lower in energy than the relaxed (1×1) surface can be seen in Fig. 2(b). The dimer atoms and corner atom all serve to reduce the energy much as the dimer-row model predicted. Also many of the first-layer atoms on both the faulted and unfaulted sides help to reduce the energy. A likely reason for this is that the dimer rows tended to cause a tensile stress relative to the 1×1 surface and those atoms bonded to the dimers were most affected. The added effect of the corner hole gave those atoms both near the corner and the dimer rows an advantage.

These figures strongly support the premise of the dimer-row model.[11,18,19] In particular, the dimer rows are seen to be very important to the reduction in energy of the DS surface when it is compressed. The corner hole atom is also seen to contribute to a decrease in energy under compression. It may have been assumed, but it is interesting also to note the contribution of many of the first-layer atoms to the reduction in energy. These first-layer atoms are principally the ones near the dimer rows.

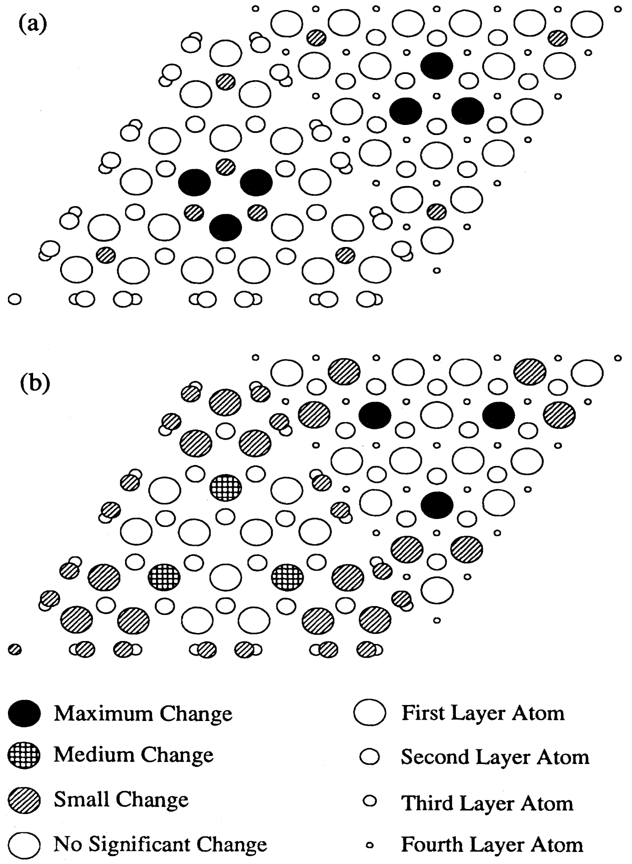

FIG. 2. (a) Energy changes per atom for those atoms which tended to increase the overall energy of the 7×7 DS surface relative to the 1×1 surface when both were under compressional strains. (b) Same as (a), but for atoms which produced a decrease in the overall energy with compressional strains.

In order to further evaluate the dimer-row model, the dimensionless parameters $\tilde{c}$ and $\tilde{f}$ were found.[18,19] These parameters relate the energy of formation of the faulted surface (Δf) and the corner hole (Δc) to the energy of formation of the dimer rows (Δw). According to the model, Δw should be negative. $\tilde{f}$ and $\tilde{c}$ are Δf and Δc divided by the absolute value of Δw. The method of determining these from the energies of the 5×5 (as 10×10), 7×7, and 9×9 DS surfaces is found from[19]

$$\Delta E = \frac{1}{2}\Delta f + \frac{2n}{(2n+1)^2}\Delta w + \frac{1}{(2n+1)^2}\Delta c \qquad (5)$$

where ΔE is the energy for the 5×5, 7×7, or 9×9 surface. n is determined by the geometry of the cell as $(2n+1)\times(2n+1)$; for 5×5, 7×7, and 9×9, n is 2, 3, and 4. The values for Δf, Δw, and Δc were 0.15, -1.17, and 4.184 eV, respectively. Each of these is about twice the value found in Ref. 19 for silicon. Also the faulted energy found here is larger than the energy for the faulted surface listed in Table III.

The values for $\tilde{f}$ and $\tilde{c}$ came out to be 0.13 and 3.57. In the dimer-row model, these values place the germanium surface under normal conditions in the 1×1 region above the 9×9 DS region.[19] When adatoms are included this would translate into the $c(2\times8)$ region above the 9×9 DAS region. This is propably because the energies found in the present model for the 7×7 and 9×9 DAS surfaces were closer than they should be.

The most likely reason for the germanium surface, under ideal conditions, to prefer the $c(2\times8)$ arrangement is that it finds less energy gain in forming the dimer rows relative to the stress associated with the dimer rows than silicon does. This can be seen from the comparison of the (1×1) relaxed and (7×7) DS surfaces. The former has a lower energy in Ge(111), but a higher energy in Si(111). It is interesting to note, though, that the surface stresses of the 2×2 surfaces of Si and Ge show that the Ge surface is under less stress.[10] Certainly, the added stress of the dimer rows seems to be the likely reason that germanium does not form a DAS surface.[18,19] These two stresses appear to be too large for any energy gain in reducing dangling bonds by forming dimer rows. It is not until the surface is compressed or relieved by other atoms that the stress is changed sufficiently so that the associated energy drops and the DAS models can develop.

The effect of the adatoms seems to be quite small. As indicated, the transformation appears to be moved some, but this is probably due to the added effect of the adatoms on the surface stress. The overall behavior of the per atom energies seen for the adatom-free surfaces is not expected to change significantly with the addition of adatoms. The only exception to this might be the movement of the first-layer atoms bonded to the adatoms and the rising out of the plane and the increase in charge of the rest atoms.

IV. STRAINED Si(111)

Assuming that silicon and germanium are alike, it would be expected that under expansion the silicon surface might transform into a simple adatom surface such as $c(2\times8)$. Some experiments possibly see such a transformation.[4,14] The dimer-row model has been used to predict that this transition occurs as, basically, the reverse of the germanium transition and, furthermore, that it occurs at approximately 1% expansion.[11] It would be useful to perform this calculation in the context of a tight-binding model for a uniform treatment and analysis of electronic changes.

A. Calculations

The overall procedure for the expansion of the silicon surfaces was the same as that used for the germanium compression calculations. Again the two-dimensionally expanded bulk was relaxed in the third dimension and these energies are in Table IV. The hydrogen-silicon layer was kept fixed and the H-Si parameters given in Sec. II were used.

B. Results

The results for the adatom free surfaces are shown in Fig. 3(a). The figure looks very different from Fig. 1(b), which was for the adatom-free germanium surfaces. The rapid drop in the relaxed (1×1) energy at higher lattice constants is due to the rapid increase of the bulk energy in Table IV. The Ceperly-Alder (CA) exchange correlation,[37] which was used in the *ab initio* calculations from which the silicon parameters were derived,[20] is partly responsible for this behavior. It is known that the CA correlation tends to produce a larger bulk modolous than the Wigner correlation.[38] This would cause the bulk energy to rise rapidly under strain much as it has done here. On the other hand, the total energy of a surface seems to be rather level or drop causing the surface energies to look unusual and possibly producing high stresses. For instance, the stress of the relaxed (1×1) surface here is about -0.73 eV/(1×1). Yet when Fig. 3(a) is compared to Fig. 1(b) it can be seen that in the compressed region (the region to the left of the ideal lattice constant) silicon has a smaller slope than the germanium relaxed (1×1) surface. The rapid drop on the expanded side for silicon is part of the reason that surface stress is larger than the value $[-0.25$ eV/$(1\times1)]$ found for germanium. When the silicon value is compared to the *ab initio* value using the Wigner correlation of -0.5 eV/(1×1),[11] the possible effect of the correlations must be remembered. Another possibility for the stress error may arise from the fewer number of layers used for the silicon calculation. However, it is certain that the extra layers would not change the rapid drop in formation energy seen in Fig. 3(a) since this depends on the bulk energies. All values will be reported as they are and the possibility of adjustment kept in mind.

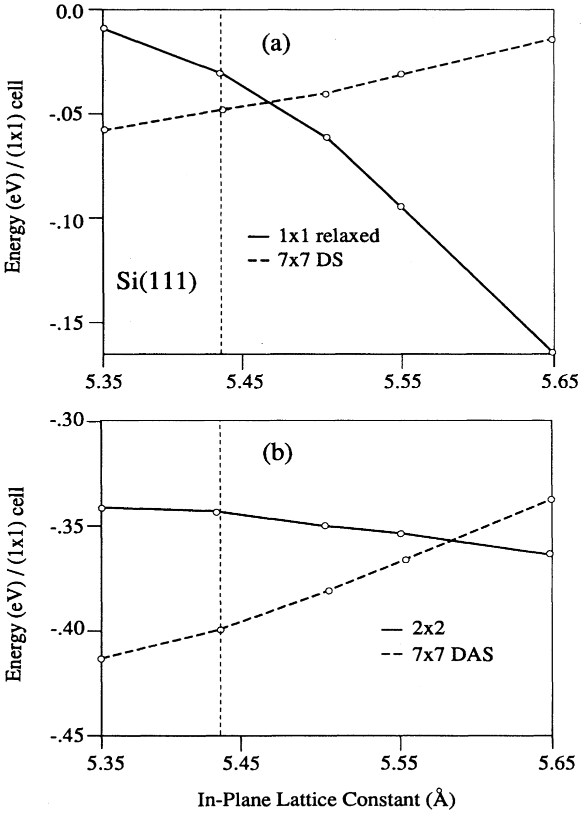

FIG. 3. (a) Energy per (1×1) for two adatom-free silicon (111) surfaces as a function of in-plane lattice constant. The ideal lattice constant is a vertical, dotted line. (b) The same surfaces as in (a) with adatoms.

Since the present silicon total-energy model applies this high stress behavior to all surfaces calculated, the relative energies and other results should be quite good. In Fig. 3(a), a transition between the relaxed (1×1) and the 7×7 DS surfaces occurs at about 0.5% expansion over the normal silicon lattice constant. As predicted,[11,18,19] the 7×7 DS surface is under tensile stress and rises in energy with the expansion. This surface stress is about 0.40 eV/(1×1), which is smaller than the values given by classical analysis.[11]

The adatom surfaces are shown in Fig. 3(b). The two adatom surfaces have been corrected for their adatom coverage by Eq. (1). The cross over between the 2×2 and 7×7 DAS surface is seen to occur at about a 2.5% expansion from the ideal lattice constant. This shows a noticeable increase over the adatom-free surfaces and an increase in the adatom effect seen for germanium. However, it is apparent that the transition for silicon would occur with or without adatoms; the major contribution of the adatoms is to reduce the surface energy by reducing the number of dangling bonds. The surface stresses for the 2×2 and 7×7 DAS surfaces are ≈0 and 0.54 eV/(1×1). For the 2×2 surface this is far below the value of 1.66 eV/(1×1) given by *ab initio* work.[10] Evidently the strain dependence of the adatoms is also not well described. The error seems to be much larger than that seen for the germanium 2×2 surface. Differences between the silicon and germanium errors can probably be related to the difference in orbitals and bonds between the two elements and the corresponding effects that these had in determining the parameters for the models. Since the 2×2 surface needs some adatom strain correction it is quite likely that the 7×7 DAS surface also needs one since the triangular island regions are locally 2×2. Again, as for germanium, the corrections to the stresses would nearly cancel each other and the overall result for the transition would be the same.

C. Analysis

Because of the large change in energy of the 1×1 surface on expansion the comparative method used for germanium was not effective for silicon. Instead the E_{bs} per atom and the repulsive energy per atom were found and added to give the total energy per atom. The difference between the total energy per atom at 5.43 Å and 5.65 Å was then determined. This difference is depicted in Fig. 4, which combines both positive and negative energy changes into one plot. The majority of atoms are white; this represents small or insignificant changes. The hatched atoms represent a much larger increase in energy. No atoms with appreciable energy decrease were found.

There is little difference between the silicon total energy for the DS surface and the results for the total relative energy for germanium that was depicted in Fig. 2. With expansion a number of the atoms associated with the dimer rows increased the energy of the DS surface just as many of these same atoms decreased the energy for germanium under compression. Certainly, these include a number of the dimer atoms themselves. The dimer atoms can be seen to be getting further from each other and from some of the first-layer atoms attached to them. This tended to raise the energy of these atoms. Additionally, the first-layer atoms near the corner holes show an increase in energy. This is predominately due to the stress of this arrangement on the first-layer atoms and probably the second-layer atoms which act as a link to the corner hole.

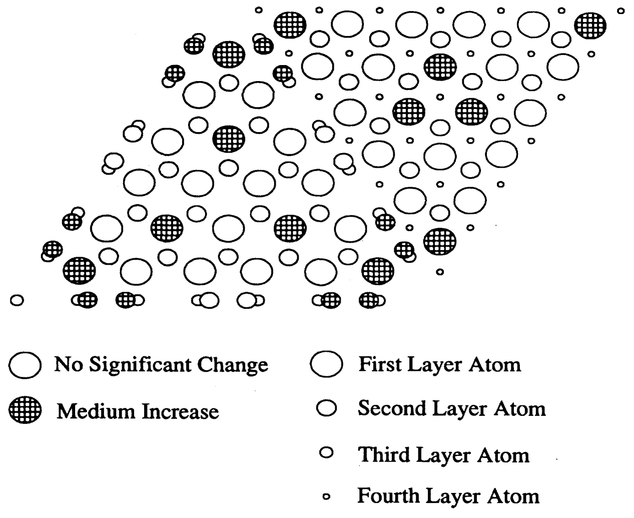

FIG. 4. The change in energy per atom (relative to 1×1) for the silicon 7×7 DS surface under expansive strain.

Surprisingly the interior of the unfaulted side shows an increase in energy. The two triangular regions both showed a drop in the repulsive energy, indicating that it was the E_{bs} energy which rose more for the unfaulted side than the faulted. Therefore as the surface expanded the unfaulted side developed a number of higher-energy electronic states, while the faulted side was able to reduce this effect to some extent because it was faulted. This may not seem reasonable since the unfaulted side is, at the ideal lattice constant, under compressive tension indicating that it would like to expand. However, as could be seen in the germanium relaxed (1×1) energy plot [Fig. 1(b)], the unfaulted surface [which is the relaxed (1×1) surface] would begin to rise in energy with sufficiently large expansions. It would seem that this is the case here. The faulted side due to its different atomic arrangement was able to reduce the strain effects enough in this interior region to not be a major contributor to the rise in energy.

V. CONCLUSION

In most cases, the silicon and germanium surface calculations agreed very well with *ab initio* results when available. Errors in the absolute surface energies and stresses were discussed. The atomic arrangements, charge distributions, and relative energies within "groups" was excellent. Also such things as buckling of the π surfaces and asymmetries in the $c(2\times8)$ surfaces were seen. The exception to good results was the error between groups of different adatom concentrations. It seemed that highly nonsymmetric bonding with the possibility of d orbitals was a problem to model. This was corrected by adding a simple adatom energy term producing very similar results to *ab initio* calculations; however, more substantial changes to the model could be made. The silicon and germanium surfaces also showed a good ordering for the lowest-energy structure. In general, the current model seemed able to describe a wide range of silicon and germanium surface properties.

The compression of the germanium surface led to the transformation of the Ge(111) surface from $c(2\times8)$ to 7×7 DAS at about 1.5% of the lattice contraction. Without adatoms the germanium surface was still seen to change from a 1×1 pattern to a 7×7 DS pattern at about 3%. This verifies the predictions of the dimer-row model[11,18,19] and agrees with the findings of experiment.[17] The change in transition point indicated that the adatoms possibly played some role in determining the location of the transformation. The percent change in transition is not neglible, but the transition pattern is not affected. An analysis of the energies per atom showed that the dimer rows and the atoms surrounding them were very important in reducing the energy of the 7×7 DS surface relative to the relaxed (1×1) surface. Also those atoms near the corner holes also tended to lower the relative energy.

A similar calculation involving the expansion of the Si(111) surface also showed a transformation from the 7×7 DS surface to the relaxed (1×1) surface. The expansion of 0.5% was in agreement with the predictions of the dimer-row model. With adatoms the needed expansion changed to about 2.5%, indicating again the role that adatoms play in the transformation. Surface stresses for the adatom surface again indicated a need for a strain correction. Finally, the analysis of the energy per atom for the 7×7 DS surface under expansion showed few differences to that found for germanium; the dimer rows, the corner hole, and associated atoms tended to raise the energy under expansion.

ACKNOWLEDGMENTS

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