

RELAXATION OF (111) SILICON SURFACE ATOMS FROM STUDIES OF Si_4H_9 CLUSTERS¹A. Redondo,² W. A. Goddard III,³ T. C. McGill⁴ and G. T. Surratt⁵Arthur Amos Noyes Laboratory of Chemical Physics⁶ and
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Self-consistent Hartree-Fock and generalized valence bond calculations have been performed on clusters modeling the (111) silicon surface. We find that the surface state is accurately described as a dangling bond surface orbital with 93% p character. We determined the optimum relaxation of the surface layer to be 0.08 Å toward the second layer. In the positive ion, the surface atom relaxes toward the second layer by an additional 0.30 Å, and for the negative ion the surface atom moves toward the vacuum 0.25 Å. The vertical ionization potential was found to be 5.78 eV (experimental values are 5.6 - 5.9 eV) while the calculated adiabatic electron affinity is 3.02 eV.

1. Introduction and Summary of Results

THE PROPERTIES OF solid-gas and solid-solid interfaces play a crucial role in such diverse phenomena as modern semiconductor devices and heterogeneous catalysis; however, concrete knowledge of the microscopic characteristics of the surface states is only now emerging. A case of particular interest is the (111) surface of Si which exhibits rearrangements of the surface atoms resulting in both 2×1 and 7×7 patterns. As a first step in learning about such rearrangements we have studied the relaxation of a (111) surface atom for the case of a neutral surface and for a surface in which one electron has been added or removed. The basic approach in these calculations is to model the surface in terms of a finite complex of atoms and then to use *ab initio* based techniques of quantum chemistry to solve for the wavefunctions.

Our results for the Si_4H_9 complex (de-

scribed below) are summarized in Table I. For the neutral surface we find that the surface atom moves toward the bulk 0.08 Å (10% of the interplanar distance), leading to a new Si-Si bond length of 2.33 Å (compared to 2.35 Å in the bulk). The resulting dangling bond orbital is shown in Figure 1a. It is localized in the region of the surface atom (93.1%) and is mainly p-like (92.9%). We also calculate an energy of 0.036 eV to excite the symmetric (C_{3v}) vibrational level.

For the positive ion the surface atom moves toward the bulk by an additional 0.30 Å (a total relaxation of 48% of the interplanar distance). The new Si-Si bond length is 2.25 Å. The resulting vertical ionization potential is 5.78 eV which is to be compared with experimental values of 5.6 eV to 5.9 eV.⁷ Allowing the ion to relax to its new equilibrium position leads to an energy decrease of 0.30 eV giving an adiabatic ionization potential of 5.48 eV.

Table 1. Summary of quantities relating to the Si_4H_9 cluster model of the Si (111) surface.

	Neutral	With dielectric corrections		Without dielectric corrections	
		Positive Ion	Negative Ion	Positive Ion	Negative Ion
Relaxation (Å) ^a	-0.08	-0.38	0.17	-0.36	.23
$R_{\text{Si-Si}}$ (Å)	2.33	2.25	2.41		
Energy (eV) ^{a,b}	-0.024	+5.459	-3.038	+7.382	-0.643
$\bar{h}\omega_0$ (eV) ^c	0.036	0.030	0.030		

^a With respect to the ground state of the neutral at the undistorted positions on the surface Si. Negative distance value indicates motion toward the bulk.

^b Calculated total energies are (in Hartree atomic units) -20.04811, -19.84663, -20.15890, -19.77596, -20.09155 respectively.

^c Energy necessary to excite the first symmetric C_{3v} vibrational state (obtained by solving numerically for the first two vibrational levels in the calculated one-dimensional potential).

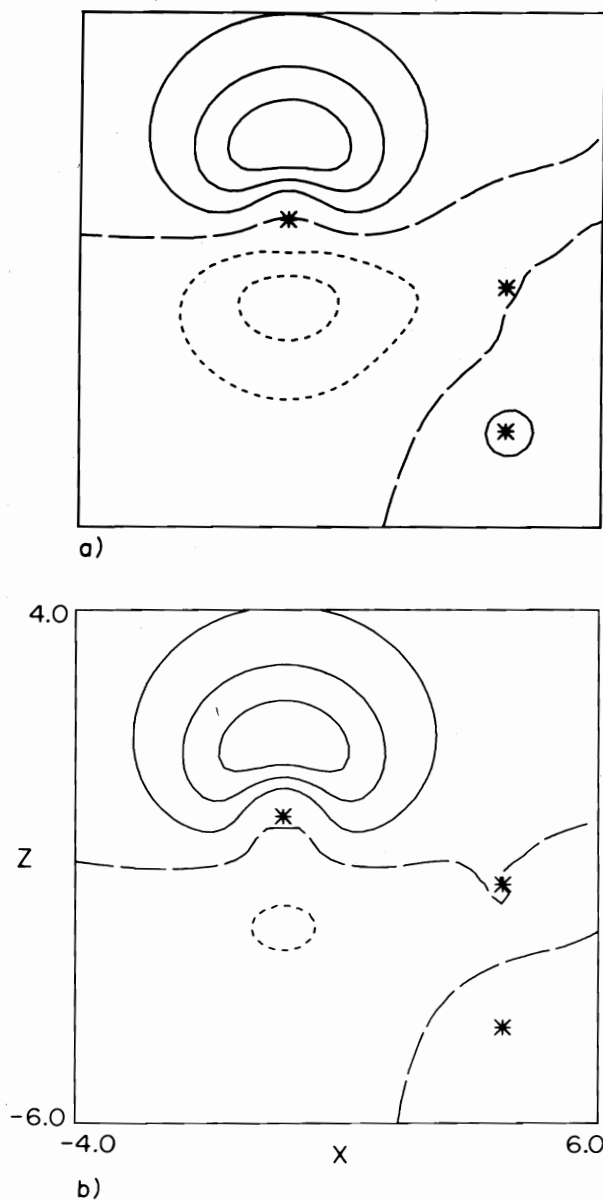


Fig. 1

- (a) Dangling bond orbital (ϕ_{13}) for the neutral complex.
 (b) Dominant natural orbital (ϕ_{13}) for the dangling-bond electron pair of the negative ion.

The z axis is oriented perpendicular to the surface. Each asterisk indicates the location of an atom in the plane of the plot. Long dashes indicate the nodal plane. Other contours are at uniform increments of 0.05 a.u. in orbital amplitude.

A calculation of the Franck-Condon factors shows a full width at half maximum of 0.3 eV arising from Franck-Condon overlap effects. (The experimental width is ~ 0.75 to 0.8 eV⁷ and presumably also includes resonance broadening due to electronic interactions with the states of bulk bands.)

For the negative ion we find that the surface atom moves away from the surface by 0.25 \AA

(from the location of the optimum neutral surface), leading to a new Si-Si bond length of 2.41 \AA . The calculated adiabatic electronic affinity (EA) is 3.02 eV.

2. Computational Details

The complex used to represent the (111) surface consists of four Si atoms and nine H atoms. There is one surface Si atom bonded to its three Si nearest neighbors in the plane immediately below. These three "bulk" silicons each have as nearest neighbors one Si (the surface Si) and three hydrogen atoms. An Si-H bond length of 1.48 \AA was used.⁸ The main reason to introduce the hydrogen atoms is to eliminate dangling bond orbitals in the "bulk" part of the complex that otherwise would couple with the orbitals of the "surface" part of the complex. The geometry chosen is that of the tetrahedral bulk configuration except that the position of the surface atom was varied along the $[111]$ direction (threefold axis). The range of the variation was from $-0.8 a_0$ to $0.6 a_0$ (a positive displacement implies motion away from the surface).

The ten core electrons of the silicons have been replaced by an effective potential (described elsewhere⁹) constructed from *ab initio* calculations on the Si atom. Comparisons in smaller systems⁹ with full *ab initio* calculations show that the excitation energies and ionization potentials are affected less than 0.1 eV by the use of this effective potential. The basis set employed in these calculations is an optimized "double zeta" basis⁹ consisting of 20 gaussian basis functions on each Si contracted down to eight and three gaussians on each H contracted down to two. For smaller complexes we tested the inclusion of d polarization functions and found their effect to be small.^{10,11}

An important consideration is the form of the wavefunction used. The neutral complex is a doublet state and we carried out fully self-consistent open-shell Hartree-Fock (HF) calculations for this state. The wavefunction has the form

$$\mathcal{A}[(\phi_1\phi_1\alpha\beta)(\phi_2\phi_2\alpha\beta)\cdots(\phi_{12}\phi_{12}\alpha\beta)(\phi_{13}\alpha)] = \mathcal{A}[\phi_{\text{bulk}}(1,\dots,24)\chi_{\text{bulk}}(1,\dots,24)\phi_{13}(25)\alpha(25)] \quad (1)$$

(12 doubly-occupied bonding orbitals plus the dangling bond orbital ϕ_{13}) where \mathcal{A} is the antisymmetrizer or determinant operator. The positive ion is a closed-shell singlet state and the corresponding closed-shell HF calculations were performed. In this case the wavefunction is

$$\mathcal{A}[\phi'_{\text{bulk}}(1,\dots,24)\chi_{\text{bulk}}(1,\dots,24)] ,$$

where the prime indicates that the optimum orbitals ϕ_1 to ϕ_{12} are not the same as (although very similar to) those of (1).

For the negative ion state the HF description would be to place the new electron in ϕ_{13} with spin β and to solve self-consistently. In order to be consistent with (1), it is necessary to include also the additional electron correlation effects due to the second electron in ϕ_{13} . This we have done by employing a generalized valence bond (GVB) wavefunction.¹² To

properly correlate the doubly-occupied dangling bond orbital, we have introduced three correlating orbitals. The new wavefunction takes the form

$$A \left\{ \phi_{\text{bulk}}''(1, \dots, 24) \chi_{\text{bulk}}(1, \dots, 24) \phi_{\text{surf}}(25, 26) \times \alpha(25)\beta(26) \right\}, \quad (2)$$

where

$$\begin{aligned} \phi_{\text{surf}}(25, 26) = & C_{13}\phi_{13}(25)\phi_{13}(26) + \\ & C_{14}\phi_{14}(25)\phi_{14}(26) + C_{15}\phi_{15}(25)\phi_{15}(26) + \\ & C_{16}\phi_{16}(25)\phi_{16}(26). \end{aligned}$$

All 16 orbitals are then solved for self-consistently. Physically the additional terms in (2) describe in-out and angular correlations of the electrons. This is accomplished by the fact that the normalized orbitals ϕ_{14} to ϕ_{16} have appropriate nodal planes in the regions where ϕ_{13} has a large amplitude. The energy obtained with the wavefunction (2) is 0.35 eV lower than that of the corresponding HF wavefunction for the negative ion. [The coefficients C_{14} to C_{16} have values between 0.04 and 0.08 whereas C_{13} has a value of 0.995.] Since negative ion orbitals often need to be more diffuse than their counterparts for the neutral systems, we also included four additional diffuse functions^{9,11} on the surface silicon. The orbitals ϕ_{13} for the neutral and the negative ion are plotted in Fig. 1.

In the calculations described above we have used no empirical parameters or other adjustments. For the neutral state it is expected that our calculated geometry is quite close to the geometry that one would obtain with an infinite complex.

For the positive and negative ion states a point charge on the surface of a semi-infinite solid leads to polarization effects extending over a large volume and decreasing slowly with distance. In this case our use of a finite complex is expected to lead to large systematic errors in the IP and EA. To estimate these effects we corrected the SCF calculations using a simple model from classical electrostatics. We considered that we had described all polarization effects within a hemisphere of radius r_0 (corresponding to the surface complex) and calculated the change in free energy¹³ for a semi-infinite dielectric with a hemispherical cavity (at the surface) and a charge of one electron located at a position h above the surface silicon. The radius r_0 was taken as the Si-Si distance, and the location $h = 0.805 \text{ \AA}$ was found by evaluating $\langle z \rangle$ and $\langle z^2 \rangle$ for the dangling bond orbital. The results with and without these corrections are listed in Table I. Considering variations in the various quantities over reasonable ranges, we estimate that the correction energies are accurate to 0.3 eV.

In the above calculations the initial (undistorted) geometry was based on the experimental geometry of the solid ($R_{\text{Si-Si}} = 2.35 \text{ \AA}$). In order to obtain an estimate of the error in bond lengths to which our calculations should lead, we carried out similar calculations for H₃Si-SiH₃; here we found the optimum distance to be $R_{\text{Si-Si}} = 2.35 \text{ \AA}$, whereas the experimental

value¹⁴ is $R_{\text{Si-Si}} = 2.33 \text{ \AA}$. Thus our calculations can be expected to overestimate the bond length by 0.02 \AA . Correcting our calculations for this leads to a relaxation of 0.13 \AA rather than 0.08 \AA . On the other hand, in our relaxation calculations we allowed only the one surface Si to relax. Repeating our calculations and letting the six hydrogen atoms representing other surface Si atoms also relax a proportional amount reduces the calculated relaxation from 0.08 \AA to 0.03 \AA . Combining both corrections leads to a corrected relaxation of 0.08 \AA ; thus no change.

3. Discussion

Except for the IP of the Si surface (*vide supra*) there are as yet no experimental results with which to compare our calculations. Recently, pseudopotential band calculations^{15a,c} and χ calculations^{15b} have been reported on models for relaxed and unrelaxed (111) silicon surfaces. However, these methods did not allow for evaluation of the total energies and hence the optimum distortions could not be calculated. One approach^{15a} to estimating the relaxation has been to use Pauling's formula¹⁶ relating bond lengths to bond order, assuming surface bond orders of 1/3. This leads to a relaxation of 0.33 \AA towards the second layer, four times our calculated number. The use of this formula gives too small a bond length because the dangling bond orbital cannot effectively participate in the bond.

We calculate that the excitation of the vibrational mode in which a single surface Si atom moves vertically to the surface occurs at 0.036 eV. In order to determine how accurate this quantity is, we used the same procedure to determine the Si-Si stretch of disilane (H₃Si-SiH₃); we obtained 0.055 eV as compared with an experimental value of 0.054 eV.¹⁷ Thus our calculated surface vibrational frequency should be reliable. Unfortunately, the transition is probably weak and broad due to interaction with the bulk phonon states of the solid. Ibach *et al.*^{18a} have observed experimentally a "surface" vibrational excitation of 0.056 eV. It appears to us that they were mainly exciting the LO phonon band of the bulk along the [111] direction, which has a spread of 0.052 to 0.064 eV.^{18b}

Although we have included the dominant correlations in the dangling bond electron pairs of the negative ion, there are additional electron correlation effects involving simultaneous excitation of the dangling bond pair and the orbitals of the complex. Inclusion of these effects would increase the EA with only minor effects on the geometry.

To our knowledge this is the first calculation in which the relaxation distances for a model of the silicon surface have been optimized by minimizing the total energy of the system. We are currently carrying out similar calculations on complexes chosen to model the (100) and (110) surfaces and steps on various silicon surfaces. We are also considering larger complexes required to examine the 2 × 1 rearrangement of the Si (111) surface.

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$$\delta F = -\frac{1}{4} \left(\frac{\epsilon - 1}{\epsilon + 1} \right) \frac{1}{h} \left\{ \frac{h}{r_0 + h} - \log \left(\frac{\sqrt{r_0^2 + h^2}}{r_0 + h} \right) \right\}$$
 where ϵ is the dielectric constant.
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