

Electronic structure of steps on silicon (111) surfaces from theoretical studies of finite clusters

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Generalized valence-bond and configuration-interaction calculations were carried out for models of the steps on (111) surfaces. A characteristic of the step is a divalent Si atom adjacent to a trivalent surface Si atom. The result is three localized electronic states separated by less than 0.3 eV. These states have quite different electronic structure than the surface dangling bond, and they are expected to be reactive toward a large range of chemical species.

An important aspect of real cleaved semiconductor surfaces is the presence of steps. Such steps lead to significant modifications of the electronic and mechanical properties and the chemical reactivity,¹ as compared with the behavior expected of an ideal cleaved surface. The elucidation of the microscopic structure at steps has proved elusive due to significant experimental and theoretical difficulties. Experimentally, major difficulties are reproducibility in forming steps and in separating the properties due to the steps from those of the perfect surface and the bulk. Major theoretical problems are (i) the lack of symmetry (even lower than that of a perfect surface) and (ii) the importance of electron correlation effects in the resulting localized electronic states. Previous studies² have overcome the first problem, including a semi-infinite or slab geometry accounting for an infinite number of atoms. However, these approaches are based on Hartree-Fock-type wave functions that cannot include the specific electron correlation effects important for localized electronic states. (For example, we find that the Hartree-Fock description of the step leads to a triplet ground state, whereas inclusion of electron correlation effects leads to a singlet ground state.)

Our theoretical approach is to include the electronic correlation explicitly but to replace the semi-infinite solid with a finite cluster of atoms. As we have shown in similar systems,^{3,4} such a treatment accounts for the major electronic (localized states) and geometric characteristics.

In this paper we present theoretical calculations for several models of steps on the (111) surface, all involving divalent silicon atoms (that is, silicon

atoms bonded to only two nearest neighbors). These divalent silicons present characteristic electronic configurations quite different from the trivalent dangling-bond states of a perfect (111) surface. First we consider the simplest model of a divalent surface Si atom.

Isolated divalent surface state. Consider a silicon bonded to two tetravalent Si atoms as, for example, occurs on the unreconstructed Si(100) surface. The simplest model for this configuration is $\text{H}_3\text{Si}-\ddot{\text{Si}}-\text{SiH}_3$, where the bulk Si are fixed at the normal tetrahedral positions but the surface Si (divalent) is allowed to relax. This particular configuration results in two low-lying states [see Fig. 1(a)].

³($\sigma\pi$). Of the two nonbonded valence electrons, one is in a *p*-like orbital perpendicular to the Si-Si-Si plane (this is denoted as π and indicated schematically in Fig. 1 by a circle; visualize an orbital sticking out of the paper) and the other is in an sp-hybrid orbital in the plane (this is denoted as σ and indicated in Fig. 1 by a lobe). (The hybridization⁵ of the σ orbital is $s^{0.20}p^{0.68}d^{0.01}$.) The orbitals are coupled into a triplet state, hence the state is denoted as ³($\sigma\pi$). There is also a $\sigma\pi$ state with both electrons coupled into a singlet spin ¹($\sigma\pi$), lying 1.30 eV above ³($\sigma\pi$) (roughly twice the $\sigma\pi$ exchange integral). The optimum bond angles for these states are 111.5° for the triplet and 111.7° for the singlet, corresponding to a displacement of the surface atom of 0.05 Å from the unrelaxed tetrahedral position (toward the bulk, away from the vacuum). Electronic correlation effects in the $\sigma\pi$ states are of minor importance.

σ^2 . In the simplest description both nonbonded

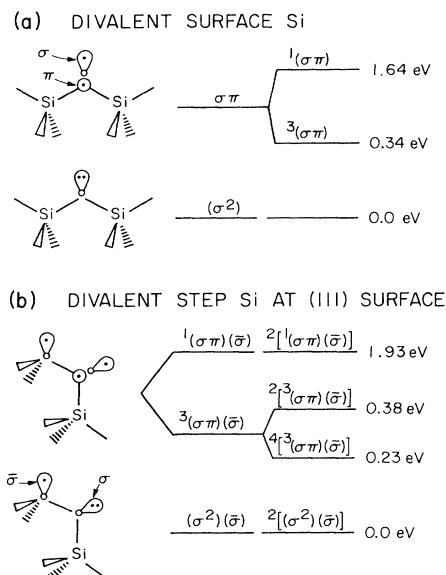


FIG. 1. Schematic of the electronic structure of (a) the $\text{H}_3\text{Si}-\ddot{\text{Si}}-\text{SiH}_3$ complex and (b) the $\text{H}_2\ddot{\text{Si}}-\ddot{\text{Si}}-\text{SiH}_3$ complex. A circle \bigcirc represents a p -like orbital coming out of the plane of the paper; a lobe ∞ represents a σ orbital in the plane of the paper; dots denote the number of electrons for each orbital. The energy separations are for the ground-state geometry and are not to scale.

valence electrons are in σ orbitals; however, including correlation effects^{4,6} we find one electron is in an orbital pointing above the Si-Si-Si plane ($\sigma + \lambda\pi$) with the other electron in an orbital pointing below the Si-Si-Si plane ($\sigma - \lambda\pi$). These orbitals are spin-paired into a singlet state and the final hybridization⁵ of each orbital is $s^{0.44}p^{0.53}$. The optimum bond angle is 105.4° , corresponding to a displacement of the surface atom of 0.10 \AA from the unreconstructed tetrahedral geometry (toward the vacuum). Electron correlation effects are of crucial importance here. Without them (i.e., Hartree-Fock) the σ^2 state is above the $^3(\sigma\pi)$ state (by 0.23 eV), but including correlation, the σ^2 state is the ground state (by 0.34 eV).⁷ The adiabatic separation between σ^2 and $^3(\sigma\pi)$ is 0.18 eV .

These states are analogous to the states of the methylene molecule $(\text{CH})_2$ and its derivatives, except that with carbon the $^3(\sigma\pi)$ state is generally the ground state.⁸ Few such systems are known for silicon; an example is SiH_2 which leads to a singlet (σ^2) ground state (with an optimum angle of 92°).⁹ Without the constraints of the lattice, the $\text{H}_3\text{Si}-\ddot{\text{Si}}-\text{SiH}_3$ complex leads to a σ^2 ground state (bond angle 95.2°) with the $^3(\sigma\pi)$ state at 0.49 eV

vertical excitation energy and 0.18 eV adiabatic excitation energy (bond angle 119.9°).

The divalent step configuration. When a silicon (111) surface is cleaved, two simple types of steps are possible.^{1(a)} One consists of trivalent silicon atoms (three nearest neighbors) with edges running perpendicular to the $[11\bar{2}]$ direction. The other type of step, with edges parallel to the $[\bar{1}\bar{1}2]$ direction, consists of edges of divalent Si atoms. Here we will consider the latter case¹⁰ because of the unique chemistry it possesses. Each divalent Si is bonded to a trivalent surface Si on the upper terrace of the step and to a bulk Si on the lower terrace. Thus we model this step as $\text{H}_2\ddot{\text{Si}}-\ddot{\text{Si}}-\text{SiH}_3$. In the geometry optimization, Si-Si bond lengths and the positions of the bulk Si are kept fixed; the surface and step Si atoms are allowed to move with the constraint that the SiH bonds of the upper terrace pivot in the same way as if they had been Si-Si bonds. Three low-lying states result [Fig. 1(b)].

$^3(\sigma\pi)(\bar{\sigma})$. Starting with the $^3(\bar{\sigma}\pi)$ state of the divalent Si, one can couple the $\bar{\sigma}$ dangling bond orbital of the upper terrace surface Si in two different ways, leading to quartet ($S = \frac{3}{2}$) and doublet ($S = \frac{1}{2}$) states denoted by $^4[{}^3(\sigma\pi)(\bar{\sigma})]$ and $^2[{}^3(\sigma\pi)(\bar{\sigma})]$, respectively. The overlap of the σ orbitals on these adjacent centers is quite small ($\langle \sigma | \bar{\sigma} \rangle = 0.12$), and hence the lower of the two states is the quartet; however, the doublet state is only 0.15 eV higher. The optimum Si-Si-Si angle for both of these states is 111.8° , corresponding to the step Si moving 0.09 \AA toward the bulk position. As in the $^3(\sigma\pi)$ state, correlation effects are of minor importance. The σ , π , and $\bar{\sigma}$ orbitals are plotted in Fig. 2. The hybridizations⁵ of the σ and $\bar{\sigma}$ orbitals are $s^{0.16}p^{0.74}d^{-0.01}$ and $s^{0.08}p^{0.85}d^{0.03}$, respectively.

$^1(\sigma\pi)(\bar{\sigma})$. There is one additional $(\sigma\pi)(\bar{\sigma})$ state, corresponding to the $^1(\sigma\pi)$ states of the divalent silicon. The overall spin coupling is doublet ($S = \frac{1}{2}$) and the state is denoted as $^2[{}^1(\sigma\pi)(\bar{\sigma})]$.

$(\sigma^2)(\bar{\sigma})$. The ground state (σ^2) of the divalent Si is coupled to the dangling-bond orbital ($\bar{\sigma}$) of the surface Si. Because of the presence of the less-rigid surface atom, the divalent Si is able to distort so as to decrease its bond angle to 102.7° , while allowing the surface atom to attain its preferred less-pyramidal configuration (the step Si moves 0.25 \AA away from the bulk position). Electron correlation effects are crucial here; if no correlation is included (i.e., Hartree-Fock), the ground state is $^4[{}^3(\sigma\pi)(\bar{\sigma})]$. Upon inclusion of correlation the ground state is

$^2[(\sigma^2)(\bar{\sigma})]$. The vertical excitation energies here are 0.23 eV for $^4[{}^3(\sigma\pi)(\bar{\sigma})]$ and 0.38 eV for $^2[{}^3(\sigma\pi)(\bar{\sigma})]$. Geometrical relaxation leads to adiabatic excitation energies of 0.07 and 0.26 eV, respectively. These states are shown schematically in Fig. 1(b).

Additional step configuration. A particularly interesting divalent state for a step configuration is obtained by binding a silicon atom to two adjacent Si atoms of the row of divalent Si's of the above (111) step. [Note that completing a whole new row in this way leads to the configuration observed in a (100) surface and described previously with the $\text{H}_3\text{Si}-\ddot{\text{Si}}-\text{SiH}_3$ cluster.¹¹] The result is a divalent Si bonded to two trivalent Si's, leading to a $\text{H}_2\text{Si}-\ddot{\text{Si}}-\text{SiH}_2$ complex. The low-lying states of this system are again dominated by the character of the divalent silicons. The ground state is a singlet state of the form $^1[(\sigma^2)^1(\bar{\sigma}_l\bar{\sigma}_r)]$. Here we start out with the ground state of the divalent Si (σ^2) and couple the two dangling-bond orbitals $\bar{\sigma}_l$ and $\bar{\sigma}_r$ into a singlet. Other (low-lying excited) states can be constructed in a manner similar to that of

the other complexes discussed above.

In all of the calculations mentioned above, we have used an effective potential¹² to replace the ten core electrons of each silicon atom. This has been previously tested and leads to accurate excitation energies.¹² The basis set consists of twice the number of functions as atomic orbitals (double zeta) on the Si and H atoms.¹² From studies of methylene systems, it is known that d functions are essential for a consistent description of σ^2 and $\sigma\pi$ states. Hence, all calculations include d functions on the central Si atom of the cluster. Another important aspect is the choice of the wave function. To describe the σ^2 states on an equal footing with the open-shell Hartree-Fock description of the $\sigma\pi$ states, one needs to go beyond the Hartree-Fock wavefunction. This we have done by carrying out generalized valence bond^{4,6} (GVB) calculations. In addition, for clusters including at least one trivalent Si, we carried out configuration interaction (GVB-CI) calculations⁴ allowing various excitations among the bonding and nonbonding valence orbitals (this leads to wave functions having from 44 to 142 determinants).

The electronic structure found here for the divalent step suggests that this step site is particularly reactive for a range of chemical species. In the σ^2 state the σ pair can act as a donor or Lewis base (for molecules with an appropriate acceptor site), while the empty π orbital can act as an acceptor or Lewis acid (for molecules with a donor pair). On the other hand, the presence of the two low-lying ${}^3(\sigma\pi)\bar{\sigma}$ states provide two radical orbitals for effective coupling with molecules having radical sites (singly occupied orbitals) such as O_2 , H, F, Cl, etc. Having both σ^2 and $\sigma\pi$ states within 0.2 eV of each other, these step sites should be considerably more reactive than the sites of the perfect (111) surface. (As would be expected for such a reactive site, few molecules have been detected containing divalent silicons.) For either state the presence of the $\bar{\sigma}$ radical orbital on the surface Si adjacent to the step provides even greater flexibility for scission of molecular bonds. Ibach *et al.*¹³ have provided evidence that step sites on Si lead to an increase of O_2 sticking probabilities by $\sim 10^3$; this is consistent with the electronic structure at the step. (Comprehensive studies of the increased reactivity of Pt due to steps has been provided by Somorjai *et al.*^{1(d)})

In summary, we have described the localized electronic states at step sites of silicon (111) surfaces. The presence of divalent silicon atoms at

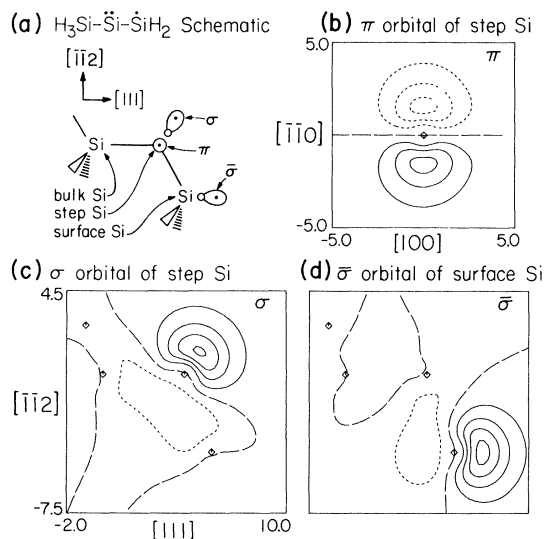


FIG. 2. Wave-function amplitudes for the $^4[{}^3(\sigma\pi)(\bar{\sigma})]$ state of the $\text{H}_2\text{Si}-\ddot{\text{Si}}-\text{SiH}_3$ complex. Note that the bulk Si is to the left. (a) Schematic of the electronic structure; (b) the π orbital at the step site; (c) the σ orbital at the step site; and (d) the $\bar{\sigma}$ orbital at the surface site. Long dashes indicate zero amplitude; solid lines indicate positive values of the amplitude; short dashes show negative values. Contours are plotted at increments of 0.05 a.u. The positions of the atoms in the plane of the plot are shown by small squares, \diamond . Distances indicated are in bohr.

these steps leads to a characteristic electronic structure. Two basic electronic configurations are present, denoted as σ^2 and $\sigma\pi$. These two configurations are modified by the presence of trivalent surface silicons, leading to sites that are expected

to be highly reactive.

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¹⁰This is the only type observed by Henzler [Ref. 1(a)] and found energetically favorable by Chadi and Chelikowsky [Ref. 2(c)].

¹¹This is a way to create a "silicon overlayer" on a (100) surface. Inserting such divalent Si atoms on alternate pairs of rows leads to 2×1 structures consistent with the observed reconstruction on prepared (100) surfaces.

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