

Step-formation energies and domain orientations at Si(111) surfaces

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Using an energy-minimization approach, we have examined reconstruction effects for one-broken-bond $[\bar{2}11]$ and cleavage-induced, two-broken-bond $[2\bar{1}\bar{1}]$ -type steps on the Si(111) surface. For a $[2\bar{1}\bar{1}]$ step, we find two inequivalent domain orientations associated with the (2×1) reconstruction pattern of the terrace atoms. Moreover, we are able to account for the relative stability of the $[2\bar{1}\bar{1}]$ step over the $[\bar{2}11]$ step. A spectral analysis of step-related state is presented and compared with recent photoemission measurements.

Steps can play a crucial role in affecting the chemical, electronic, and structural properties of intrinsic surfaces because of the generally large differences in the atomic environments of step versus surface atoms. While steps are an important intrinsic feature of cleaved semiconductor surfaces and, perhaps, in the case of Si, of the annealed (7×7) reconstructed (111) surface,¹ our understanding of the energetics of step formation and the relationship of steps to reconstruction patterns is somewhat primitive. In this paper we concentrate on the Si(111) surface, and address the questions of step formation energies, atomic relaxation, domain orientation, electronic structure, and bond strengths at steps.

The two principal step configurations on a Si(111) surface are usually denoted²⁻⁴ by $[\bar{2}11]$ and $[2\bar{1}\bar{1}]$. The primary difference between the two geometries is in the number of broken bonds at edge atoms. A $[\bar{2}11]$ step creates one broken bond per edge atom as compared to two broken bonds for a $[2\bar{1}\bar{1}]$ step. In Fig. 1, we display a simple schematic view of the two types of step configurations. A $[2\bar{1}\bar{1}]$ step involves the removal of a double layer of atoms (i.e., the edge atoms at the step correspond to "second-layer"

atoms of the ideal surface²), whereas a $[\bar{2}11]$ step can be formed by the removal of one or more double layers.³ Our calculations show that the formation of the step at the surface layer instead of at the second-layer atoms (as in Fig. 1) is, in fact, energetically very unfavorable.

A surprising aspect of step formation on the cleavage plane Si is the relative stability of the inequivalent $[\bar{2}11]$ and $[2\bar{1}\bar{1}]$ step configurations. Intuitively, a step with one broken bond is expected to be energetically more favorable than a two-broken-bond geometry. However, cleavage in the Si(111) surface always results in two-broken-bond step configurations, i.e., in a $[2\bar{1}\bar{1}]$ step.²⁻⁴ A simple argument for why the cleavage energy of the $[2\bar{1}\bar{1}]$ step should be lower than that of the $[\bar{2}11]$ step is presented in this communication.

In order to examine the $[\bar{2}11]$ and the $[2\bar{1}\bar{1}]$ step configurations, we have considered a periodic array of steps in the form of a slab. Our approach allows us to study independently the two configurations. Slab thicknesses of 6 and 12 layers and terrace widths of two atomic rows were employed. Step-step interactions resulting from our model geometry, as estimated from the small dispersion of step states along the $[2\bar{1}\bar{1}]$ direction, were minimal. We have used a parametrized tight-binding method⁵ to solve for the electronic states. Our method has been extended⁶ so that changes in the total energy resulting from bond formation or bond breaking could be calculated. The method has been previously tested in studies of surface reconstruction,⁵ and is equally well suited for examining stepped-surface geometries.

The edge atoms at a $[2\bar{1}\bar{1}]$ step are very similar to those on a Si(100) surface. These atoms bond in pairs to form asymmetric dimers with displacements which are nearly identical to those on a (100) surface. For the terrace atoms our energy-minimization calculations show three possible orientations for the (2×1) reconstructed domains at a $[2\bar{1}\bar{1}]$ step. Of these, two are inequivalent and are shown in Fig. 2. The orientation shown in Fig. 2(a) consists of raised

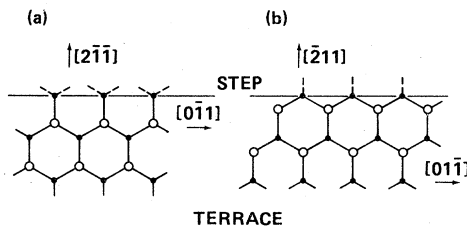


FIG. 1. Top views of two possible step geometries on the Si(111) surface. A cleavage propagating along the $[2\bar{1}\bar{1}]$ direction gives rise to a step with two broken bonds per edge atom, as shown in (a). The step configuration shown in (b), with only one broken bond per edge atom, does not result from cleavage. The surface atoms are shown as large circles and second layer atoms as small circles.

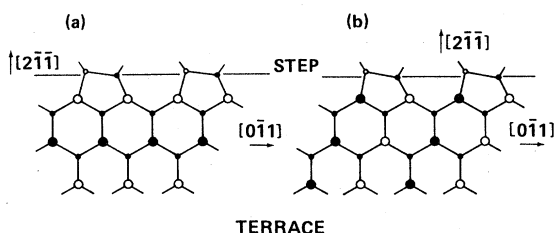


FIG. 2. Top views of two energetically favorable but structurally inequivalent orientations of terrace atoms at a $[2\bar{1}\bar{1}]$ step are shown in (a) and (b). Raised and lowered atoms are denoted by open and dark circles.

and lowered rows of atoms which are oriented parallel to the edge line. A new structure with a 60° (or 120°) orientation of the rows with respect to the edge atoms is shown in Fig. 2(b). Experimentally, low-energy-electron-diffraction (LEED) studies have established that the parallel geometry is the most predominant at the surface.^{2,7} The domain orientation is determined from the direction of broadening (or splitting) of principal-order beams caused by steps and from the position of the $\frac{1}{2}$ -order spots relative to the lines joining the integral-order spots along the direction of broadening. Domains oriented at 60° are unambiguously seen in this way on some surfaces.⁸

The magnitude of the "up" and "down" displacements of the terrace atoms for both the parallel and the 60° orientation of the rows obtained from energy minimization are found to be within a few percent of those calculated⁹ for an infinitely periodic unstepped (2×1) surface. Our results do not support the presence of an unrelaxed (1×1) region in a narrow strip of 25–50 Å near a $[2\bar{1}\bar{1}]$ step, caused by the strain field associated with the step. The possibility of a disordered and strongly reconstructed region giving rise to a (1×1) LEED pattern^{4,10} needs to be investigated more thoroughly.

A determination of which domain orientation near the step has the lowest energy is difficult. For example, it is expected that the width of the terrace could influence our results. For a terrace consisting of two atomic rows, we find that the 60° orientation [Fig. 2(b)] has a lower energy than the parallel geometry, i.e., Fig. 1(a). This result is not in strong disagreement with experiment.^{2,7} Although the parallel geometry is predominant in experiment, the 60° orientation is also seen.⁸ In addition, it is possible that the cleavage process may give rise to a non-equilibrium domain orientation.

For the single-broken-bond ($\bar{2}11$) step, a (2×1)-type reconstruction of terrace atoms also leads to a reduction in the total energy. The magnitudes of the displacements are again very similar to those calculated for the step-free (111) surface. The edge atoms at

a $\bar{2}11$ step relax inward (strengthening the back bonds) and transfer electronic charge to the nearest row of atoms on the terrace. This leads to alternate rows of raised and lowered atoms on the terrace, the edge atoms behaving as a row of lowered atoms so far as their charge state is concerned. When the number of rows (including the edge) is odd, the last row of atoms on the terrace is calculated to have an up-down pattern along the row, leading to a doubling of the unit cell along the $[0\bar{1}\bar{1}]$ direction.

The electronic structure of $[2\bar{1}\bar{1}]$ -stepped Si(111) surfaces has been previously examined experimentally^{4,10–12} and by self-consistent-pseudopotential and tight-binding methods.^{13,15} Reconstruction effects were anticipated but not included in the theoretical studies. Calculations for Si(100) and Si(111) surfaces^{5,15–18} are also relevant to the problem of the electronic structure of stepped surfaces. For the ideal, unrelaxed step geometries, our results are in good agreement with those obtained before. For the reconstructed steps, we find differences in the electronic structure of step states which depend on the domain orientation at the terrace. The calculated edge and surface electronic densities of states [for a terrace width of two atomic rows and for the 60° geometry of Fig. 2(b)] are shown in Fig. 3 and compared with experimental data. The experimental data are taken from the difference spectrum¹³ of high- and low-stepped-density surfaces obtained by Rowe *et al.*⁴ The difference spectrum enhances the step-induced changes in the density of states; it does not, however, completely reduced to zero the contribution of surface peaks. The calculated peak positions for both types of states are in good agreement (± 0.2 eV) with experiment. Our calculations show that the lowest-energy empty states which are strongly surface localized occur at nearly 0.6 eV above the valence-band maximum for both the $\bar{2}11$ and $[2\bar{1}\bar{1}]$ steps. For the case where the terrace atoms are oriented parallel to the edge atoms [Fig. 2(a)], the step-related states are found to occur 0.15 eV below the valence-band maximum (at $E=0$). These states would tend to enhance the emission near $E=0$, as is seen experimentally when the step density is increased.^{4,11}

At this point, we address the question of the relative stability of the two-broken-bond $[2\bar{1}\bar{1}]$ step configuration as compared with the one-broken-bond $\bar{2}11$ step configuration. Naively, one might expect the $\bar{2}11$ step geometry to be more stable since extra energy would be needed to create the additional broken bond of the $[2\bar{1}\bar{1}]$ step. The extra energy is, in the absence of all atomic relaxations, calculated to be only 0.4 eV per bond as compared to the average energy per bond of 2.35 eV in Si. The major reason for the difference can be easily understood from the following simple tight-binding description.

A dangling bond on a $\bar{2}11$ step atom is sp^3 in character and is similar to a dangling bond on a ter-

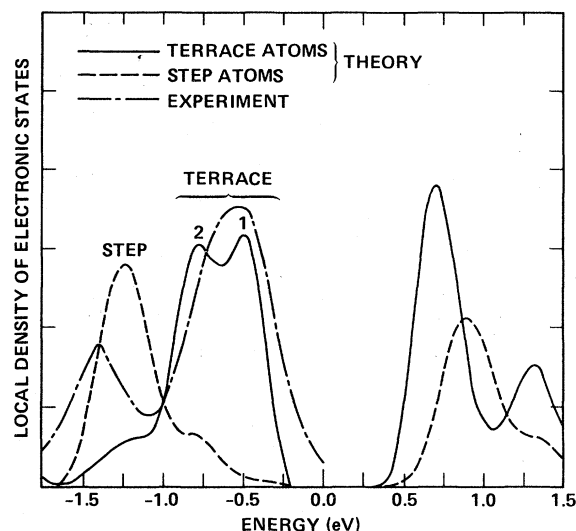


FIG. 3. The solid line shows local density of electronic states of terrace atoms. Only states having a minimum localization of 30% of their total charge on these atoms are shown. The line shows the experimental difference spectra (Ref. 4) between high- and low-stepped-density surfaces. The dashed line shows the projection of the calculated density of states onto the step atoms. The interaction between the dangling bonds at steps and at the surface splits the "terrace" density of states into two peaks. The peak labeled 1 arises from the surface dangling bonds which do not interact with the step; the one labeled 2 involves surface dangling bonds adjacent to the step.

race atom, whereas the orbital characters are very different on a $[2\bar{1}\bar{1}]$ step atom. By taking a linear combination of the two sp^3 dangling bonds on each $[2\bar{1}\bar{1}]$ step atom, a state of much lower energy can be obtained. The optimal rehybridizations result in the formation of low-energy, doubly occupied sp state [with $(s+p)/\sqrt{2}$ character] and a high-energy, empty state of purely p character. A similar rehybridization also occurs on the ideal (100) surface.^{19,20} This can be seen from the electronic charge densities obtained in pseudopotential calculations,²⁰ which show very clearly the sp and p symmetries of the two-gap states at the surface. The rehybridization from sp^3 to sp , after taking into account the effects of band dispersion, results in a significant lowering (i.e., from 2.35 to 0.4 eV) of the energy required to create the extra dangling bond at a $[2\bar{1}\bar{1}]$ step.

An analysis of $[\bar{2}11]$ and $[2\bar{1}\bar{1}]$ step-formation energies which is based solely on the extra 0.4-eV energy required to create the extra dangling bond at a $[2\bar{1}\bar{1}]$ step is deficient, however, because it neglects changes in the density-of-surface dangling bonds resulting from step formation. For simplicity, we consider a periodic step array with an angle of inclination α . We first note that cleavage leads to *identical*

step configurations on each of the two surfaces created, and we can therefore concentrate on one of these surfaces. For both the $[\bar{2}11]$ and $[2\bar{1}\bar{1}]$ step geometries, the density of step atoms n_{step} is equal to

$$n_{\text{step}} = \tan\alpha/ah, \quad (1)$$

where a is the surface hexagonal lattice constant and h is the vertical distance between two adjacent terraces. Simple geometric considerations show that the decrease in the density-of-surface dangling bonds resulting from step formation is exactly equal to

$$\Delta n_{\text{surface}} = -\frac{2}{3}n_{\text{step}}, \quad (2)$$

for a $[2\bar{1}\bar{1}]$ step and

$$\Delta n_{\text{surface}} = -\frac{1}{3}n_{\text{step}}, \quad (3)$$

for a $[\bar{2}11]$ step. Equations (2) and (3) result from the fact that steps have a finite extent which can be different for inequivalent step geometries: For a given angle α , the reduction in the density of surface dangling bonds is twice as large for a $[2\bar{1}\bar{1}]$ step as for a $[\bar{2}11]$ step. Since the bond-breaking energy at the surface is nearly 2.1 eV per bond,^{21,22} the overall cleavage energy per unit area is about $[(2.1/3 - 0.4) \text{ eV}]n_{\text{step}}$ or $(400 \tan\alpha) \text{ erg/cm}^2$ lower for a $[2\bar{1}\bar{1}]$ step than for a $[\bar{2}11]$ step. When energy lowering resulting from dimerization of step atoms at a $[2\bar{1}\bar{1}]$ step is also included, the difference in the cleavage energies is approximately $(1280 \tan\alpha) \text{ erg/cm}^2$. For comparison, the measured²¹ cleavage energy of the Si(111) surface is about 1240 erg/cm^2 as compared to a calculated²² value of 1298 erg/cm^2 . When the interactions of step and terrace atoms are also included, the above conclusions regarding the differences in the cleavage energies of the $[\bar{2}11]$ and $[2\bar{1}\bar{1}]$ steps remain essentially unchanged.

In regard to bond strengths at step atoms, our calculations show that the dimer bond energy at a $[2\bar{1}\bar{1}]$ step [or on a Si(100) surface] is only about 0.67 eV, which is significantly lower than the bulk bond strength of 2.35 eV. The reduced strength of the dimer bond is again closely related to the fact that, in breaking this bond, the resulting occupied dangling bonds are sp instead of sp^3 in character. Reduced dimer-bond strengths have been obtained in several other recent studies.²³⁻²⁶

In summary, we have used energy-minimization calculations to examine the structural and electronic properties of steps on cleaved Si(111) surfaces. The stability of $[2\bar{1}\bar{1}]$ step relative to $[\bar{2}11]$ step is found to be primarily a result of two effects: (i) A step-induced decrease in the density of surface dangling bonds which is more pronounced for a $[2\bar{1}\bar{1}]$ step than for a $[\bar{2}11]$ step, and (ii) greater electronic rehybridization effects on two-broken-bond sites. Two

inequivalent domains oriented parallel to or at 60° with respect to $[01\bar{1}]$ direction are found to be possible at a $[2\bar{1}\bar{1}]$ step. The averaged electronic states associated with the edge and terrace atoms for the two different configurations are in good agreement with experiment.⁴

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