# Nature of the Step-Height Transition on Vicinal Si(001) Surfaces

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The Si(001)2×1 surface is expected to undergo a phase transition from single- to double-atomic-height steps with increasing angle of miscut. Here we show that this transition is quite different than previously believed, involving something like a "devil's staircase" of transitions in a mixed phase consisting of a complex sequence of single and double steps. Even at low angles, where only single steps occur, the areas of 2×1 and 1×2 regions are unequal, in agreement with recent experimental results.

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Steps play a crucial role in growth at semiconductor surfaces. There has been particular interest in the role of steps of single versus double atomic height on Si(001), since single-height steps necessarily lead to antiphase boundaries in III-V semiconductors grown on Si [1]. Moreover, a series of papers by Alerhand and others [2–7] has revealed that steps on Si(001) exhibit fascinating behavior, including most notably a phase transition with increasing angle of surface miscut along [110].

Here we show that the nature of this phase transition, and the dependence of miscut angle generally, is rather different than previously believed. In particular, there is neither an abrupt transition from single- to double-height steps with angle [2–4] nor a coexistence between spatially separated regions of single- and double-height steps [5]. Instead, as the angle increases past a critical value, pairs of single-height steps collapse into double-height steps in a complex pattern, so that at zero temperature the surface undergoes a cascade of transitions resembling a "devil's staircase" [8]. In addition, even for small angles, where only single-height steps occur, the sizes of the 1×2 and 2×1 terraces are unequal. This explains the surprising recent measurements of Tong and Bennett [7].

The competition between single and double steps was first analyzed by Chadi [9], who identified the step atomic structures shown in Fig. 1. Because of the symmetry of the dimerized Si(001)2×1 surface, there are two distinct types of single-height steps, denoted $S_A$ and $S_B$. Single-height steps separate regions of 2×1 and 1×2 periodicity, so on vicinal surfaces one cannot have two $S_A$ steps without an intervening $S_B$ step, or vice versa. Since there is no corresponding restriction on double-height steps, only the lower-energy type (denoted $D_B$) need be considered [9].

Alerhand *et al.* [2] pointed out that, in order to fully understand the competition between single- and double-height steps, one must include the elastic interaction between the steps. Because of the anisotropic stress of the 2×1 surface, the energy of a flat Si(001) surface can always be lowered by introducing single-height steps, which break up the surface into domains of alternating orientation of the dimerization [6].

Single-height steps remain energetically preferred for small miscut angles. But because of the strong mutual repulsion between single steps, when the step spacing becomes too small (i.e., at large miscut angles) the energy of a pair of single steps becomes higher than that of a $D_B$ step, leading to a surface phase transition [2]. This picture was further elaborated by Poon *et al.* [4], and by Bartelt, Einstein, and Rottman [5].

From this extensive body of previous work, it is well established that there are two principal interactions between steps on Si(001), which follow directly from elementary elastic theory and the symmetry of the surface [2,4,6]. First, the anisotropic stress of the surface due to the 2×1 dimerization leads to a force monopole acting on the $S_A$ and $S_B$ step edges [6] and, consequently, a logarithmic dependence of the interaction energy on step separation [10]. Second, step edges in general may give rise to a force dipole, and for Si(001) this dipole is significant for $S_B$ and $D_B$ steps. The dipole-dipole interaction energy shows an $l^{-2}$ dependence on step separation $l$ [11]. A simple elastic model incorporating these interactions has proven to be very successful in describing the response of 2×1 and 1×2 domain sizes to an externally applied strain [6,12], and in reproducing the results of detailed atomistic simulations [4].

Here we use the same elastic model, augmented by

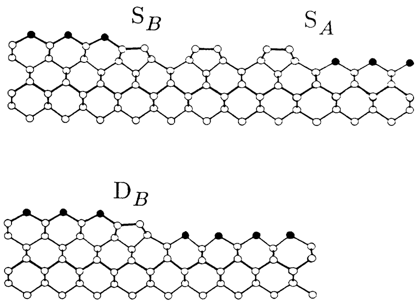

FIG. 1. Side view of the crystal structure of steps of single ($S_B$ and $S_A$) and double ($D_B$) atomic height on vicinal Si(001) surfaces. A [1$\bar{1}$0] projection is shown. Horizontal bonds are dimers of 2×1 terrace; solid circles denote dimers of 1×2 terrace, which are normal to the plane of the figure.

atomistic simulations, to show that steps on Si(001) exhibit an even richer and more complex behavior than previously recognized. We begin our analysis by considering surfaces miscut at small angles from the (001), where only single-height steps are expected. Recently Tong and Bennett [7] found that the areas of 2×1 and 1×2 terraces were unequal even at small angles. This implies either that $S_A$ and $S_B$ steps are not equally spaced, as has been universally assumed, or else that $D_B$ steps are present even at small angles.

In order to understand this behavior, we calculate the energy of a surface with a given miscut angle, and hence a given step density, as a function of the width of the 2×1 terrace. (Here 2×1 and 1×2 refer respectively to the terraces with dimer bonds perpendicular and parallel to the step edge.) The results are shown in Fig. 2(a) for a relatively small (but otherwise arbitrary) angle. The terrace-size asymmetry is immediately apparent.

Before addressing the physical mechanism responsible for the asymmetry, we should mention some details of the calculation. As we are in effect extending the work of Poon *et al.* [4], we use the same potential model, that of Stillinger and Weber [13], to permit direct comparison. However, as discussed below, the *qualitative* results may be understood from a rather general perspective, and do not depend on the precise potential. The effect of the potential on *quantitative* results is also discussed below.

Because of the long periodicity of the steps, and the corresponding depth of the strain fields, accurate numerical relaxations require enormous cells when performed with traditional methods [4]. We have therefore implemented a more efficient approach, where a few layers of atoms are coupled to a semi-infinite elastic substrate. We have used 6–8 layers of atoms, and a continuum elastic substrate incorporating the full cubic anisotropy of Si. As it is convenient to have the substrate oriented along (001), an additional double-height step is included to simulate the vicinal surface on the flat substrate. This step is fixed in a rigid ideal geometry, so that it exerts no force. Details of this method will be given elsewhere. Comparison with calculations performed as in Ref. [4] indicate that the error from these approximations is less than 1 meV/$a$ ($a = 3.84$ Å).

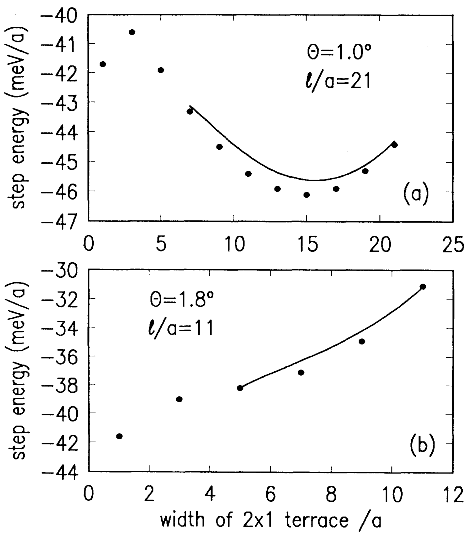

FIG. 2. Energy of a pair of $S_A$-$S_B$ steps for two fixed miscut angles $\theta$ corresponding to step separations $l$ vs the width of the minority terrace. The left-most data point corresponds to a $D_B$ step, representing the smallest possible terrace width. The right-most point is the symmetric case of equally wide 2×1 and 1×2 terraces (i.e., $p=0$). Dots are results from numerical relaxations of Si atoms interacting via the empirical Stillinger-Weber potential. Solid line is elastic continuum model, Eq. (1).

Our results, the dots in Fig. 2(a), show two local minima. The higher local minimum (left-most point) corresponds to a $D_B$ step. The configuration of minimum energy corresponds to a pair of single-height steps, with the $S_A$ step considerably displaced from the midpoint between the two neighboring $S_B$ steps (right-most dot is midpoint). Only a small barrier separates the single- and double-height configurations.

The asymmetric terraces can be understood easily within the elastic model mentioned above. Let $2l$ be the distance between two steps of the same kind, with $a$ being the surface lattice constant, and $(1-p)l$ being the size of the 2×1 terrace, so $p$ describes the asymmetry between 1×2 and 2×1 terrace sizes. Adopting Poon's notation, the parameters $\lambda_\sigma$ and $\lambda_d$ describe the force monopole and force dipole terms, with the remaining local contributions to the step energy included in a constant term $\lambda_0^{(S_A+S_B)}$. Then the energy of the step pair is

$$E=\lambda_0^{(S_A+S_B)}-2\lambda_\sigma\ln\left[\frac{l}{\pi a}\cos\frac{p\pi}{2}\right]+\lambda_d\left[\frac{a}{2l}\right]^2-(3\lambda_\sigma\lambda_d)^{1/2}\frac{a}{l}\tan\frac{p\pi}{2}\,. \qquad (1)$$

Using values corresponding [4] to the Stillinger-Weber potential, Eq. (1) gives the solid curves in Fig. 2. These continuum results agree well with the full atomistic calculations for step separations $\gtrsim 6a$. Since steps are never this close at the angles discussed in this paper, we can safely use the elastic model without further discussion.

For equal terrace sizes ($p=0$) the final term in Eq. (1) drops out, giving the expression used in Ref. [4]. However, the energy can be lowered by moving the $S_A$ step into a region of increasing displacements induced by the rebonding dipole at the $S_B$ step. For small angles this displacement of the $S_A$ step is roughly constant, approximately $5a$.

With increasing angle of miscut the $D_B$ minimum in Fig. 2 becomes deeper, until at a characteristic angle $\theta_c$ the energy of the $D_B$ minimum becomes lower in energy than the $S_A$-$S_B$ minimum, giving the transition discussed by Alerhand *et al.* and Poon *et al.* Including the terrace asymmetry changes this angle only slightly, from $\theta_c=1.1°$ to $\theta_c=1.3°$.

At still higher angles, the local minimum associated with single-height steps disappears entirely, as seen in Fig. 2(b). At such angles $S_A$-$S_B$ steps are not even metastable with respect to step displacement, but collapse spontaneously into $D_B$ steps.

We now turn to the more complex issue of the nature of the step-height phase transition, which has been the subject of recent controversy [2,3,5]. Previous analyses have invariably begun with the *assumption* that one is dealing with a transition from a phase of pure single-height steps to one of pure double-height steps. As noted by Bartelt, Einstein, and Rottman [5], in this case instead of an abrupt transition at $\theta_c$ there should occur an interval of miscut angles $\theta_1 \le \theta \le \theta_2$ where the two phases coexist (spatially separated) in thermodynamic equilibrium. The critical angles $\theta_1$ and $\theta_2$ are determined by a common tangent construction [5], which for the present parameters gives $\theta_1=0.7°$ and $\theta_2=2.0°$.

However, Alerhand *et al.* [3] argued that such coexistence of phases would require faceting of the surface, and hence substantial mass transport, which might not be kinetically allowed. If one allows local equilibration but not long-range diffusion, an abrupt transition from single- to double-height steps with angle would be expected.

Let us first examine the assumption that the phases remain pure. In that case two-phase coexistence (surface faceting) clearly gives the lowest energy, regardless of whether such a state is kinetically accessible in experiments. If, beginning from such a state, we then move one pair of $S_A$-$S_B$ steps into the $D_B$ region, we find that the energy is lowered. Thus there exists a mixed phase of lower energy than any combination of pure phases.

To show that this conclusion is rather general, we examine a simplified model. Consider two types ($a$ and $b$) of steps with dipolar interactions; i.e., the interaction energy between any two steps $i$ and $j$ is proportional to $(\lambda_d^i\lambda_d^j)^{1/2}/L_{ij}^2$, where $L_{ij}$ is the distance between the steps, and $\lambda_d^i$ can take two different positive values, one for $a$ steps and one for $b$ steps. These represent $D_B$ steps and $S_A$-$S_B$ pairs, neglecting the internal degree of freedom of the pair spacing. Then, independent of the choice of parameters, the phase with alternating $a$ and $b$ steps is lower in energy than spatially separated $a$ and $b$ phases.

So far we have only shown that what was believed to be the lowest-energy step arrangement is in fact unstable against formation of a mixed phase. To identify the structure of the minimum-energy mixed phase, we consider a given angle of miscut, and generate all possible sequences of single- and double-height steps up to a given periodicity. For each such sequence, we calculate the energy within the elastic continuum model, minimizing the energy with respect to all step positions. We then choose the step sequence with the lowest relaxed energy.

The results are shown in Fig. 3 for periodicities up to five double steps. In every case, the energy of the mixed sequence identified is lower than the energy for two-phase coexistence or for either pure phase. For angles higher than about 1.5°, the $2\times1$ area becomes rather small, and periods longer than five are needed to describe the low-energy mixed phases.

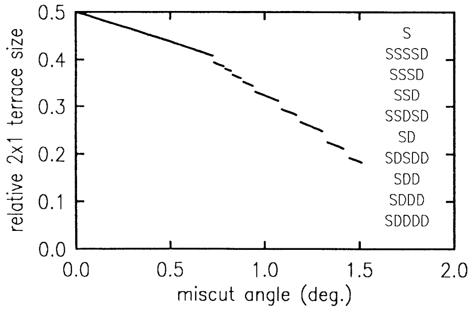

FIG. 3. Fraction of surface with $2\times1$ dimerization vs miscut angle. Patterns with periods up to five double steps are included, permitting treatment of angles up to about 1.5°. Each of the ten line segments corresponds to a distinct phase; the step orderings in the respective phases are given in the inset, where "S" denotes a *pair* of single-height steps and "D" a $D_B$ step, "SD" stands for a periodic arrangement of $S_B$-$S_A$-$D_B$ steps in that order, etc. Note that all orderings maximize the distance between single-step pairs.

The pattern of sequences in Fig. 3 is rather simple. The fraction of double steps increases monotonically with angle. For any given number of double steps, the remaining single-step pairs stay as far apart as possible, due to their strong mutual repulsion. For example, the sequence 11122 is missing in Fig. 3, while 11212, being slightly lower in energy, can be observed.

The average length of a $2\times1$ terrace (i.e., the total $2\times1$ terrace area divided by the number of single-height step pairs) remains approximately constant in the region of mixed phases, while it is, of course, rapidly decreasing with increasing angle in the pure single-height phase. Thus the behavior of the mixed phase is qualitatively reminiscent of the coexisting single- and double-height phases. Consequently, the staircase in Fig. 3 deviates only by a small amount from the almost linear curve (linear in $\tan\theta$) which one would expect in case of two-phase coexistence.

The result looks like a devil's staircase: If we could treat longer and longer periodicities, we would expect to see finer and finer structure. In fact, in the simplified model mentioned above of two steps with dipolar interactions, if we constrain the steps to be equally spaced, the model reduces to one which has been rigorously proven to exhibit a true devil's staircase of transitions [8].

The above results are strictly valid only at zero temperature; due to the small energy differences involved, the complicated ordered structures will be destroyed at temperatures where equilibration is feasible. Nevertheless, our conclusions remain relevant at higher temperatures. For the pure single-height steps which occur at small miscut angles, finite temperatures lead to thermal meandering; but this meandering takes place in a nearly symmetric potential, and so should result in little change in the average step position (and hence in the average 2×1 terrace size). Therefore the $T=0$ theory is directly applicable to the low-angle data in Tong and Bennett's experiment [7].

At higher angles, since steps already mix at $T=0$, this should remain true *a fortiori* for finite temperatures. Thus our conclusion that the equilibrium state is mixed rather than faceted or pure, with the 2×1 terrace area varying continuously with angle, remains true at all temperatures. However, as discussed by Alerhand *et al.* [2], at higher temperatures the free energy of the single-height phase is lowered by step meandering, shifting the transitions to higher angles.

Before ending, we should return to the question of quantitative accuracy. The interactions of steps on Si(001) are well described by the elastic model; but the values of the parameters in the model are not accurately known. The values used here were obtained in Ref. [4] from a specific empirical atomistic model [13]. However, we have calculated the stress anisotropy for this model, and find it to be a factor of 2 smaller than the most accurate available value [14]. This results in the crucial parameter $\lambda_\sigma$ being a factor of 4 too small. Use of more accurate parameters in the elastic model would probably shift the transitions in Fig. 3 to higher angles.

Finally, we note that at any finite temperature, along any infinite step edge in equilibrium there are necessarily both $S_A$-$S_B$- and $D_B$-like regions. Thus intermixing is expected even in the direction parallel to the steps. Figure 2 suggests a way to describe such step meandering, consistently allowing for both $S_A$-$S_B$ and $D_B$ steps within a unified one-dimensional model Hamiltonian. One simply replaces the harmonic term in the Alerhand-Poon Hamiltonian [2,4] by the full potential of Fig. 2. Preliminary Monte Carlo simulations for this model, for angles in the transition region, confirm that along the step edge there are $S_A$-$S_B$- and $D_B$-like regions. This intermixing has also been previously inferred experimentally by Tong and Bennett from their scattering profiles.

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