Equilibrium Structures of Si(100) Stepped Surfaces

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Atomistic calculations using the Stillinger-Weber interatomic potential show that stress relaxation can lower the energy of a Si(100) stepped surface below that of the flat surface. Two types of elastic interactions are identified: One is due to stress anisotropy which occurs only on single-stepped surfaces and has a logarithmic dependence on ledge separation l; the other is associated with ledge rebonding, present in both singe- and double-stepped surfaces, and has a variation of l^{-2}. On the vicinal Si(100), single-layer ledges are predicted to be favored over double-layer ledges at low miscut angles with the crossover occurring at about 1° at zero temperature, and at 3° at 500 K, in agreement with experiment.

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In the initial stage of epitaxial growth of semiconductor materials, the perfection of the substrate surface is particularly relevant since it is the template for the growth of the overlayers. The role of the surface step ledges in controlling the initial nucleation process of GaAs growth on Si has been recognized for quite some time,[1] and experimental observations of stepped Si(100) have been made with LEED and scanning tunneling microscopy (STM).[2-8] Interpretations of these findings have been based mainly on the ledge energies obtained from electronic-structure calculations using the tight-binding approximation.[9] Specifically, the *SA* ledge is predicted to be more stable than the *SB*, and the *DB* more stable than a pair of single-step ledges $(SA+SB)$.[9] These results are obtained from calculations on thin slabs of about twelve layers with semi-infinite stripe terraces separated by only a few atomic spacings. It was first pointed out by Marchenko and Parshin[10] that a step ledge can induce a line distribution of force dipoles which in turn give rise to elastic interaction between adjacent ledges. Furthermore, Marchenko[11] has shown that on a surface with alternating stress domains, stress relaxation will lower the energy of the surface. The single-stepped surface of Si(100) is such an example, where the stresses on the upper and lower terraces are not equal due to different orientations of dimerization.

Recently, Alerhand *et al.*[12] have considered the effect of elastic interaction on a single-layer step ledge for variable ledge separations, and concluded that the Si(100) surface will be the single-stepped surface whenever the defect energy associated with ledge formation is offset by the effects of stress relaxation. Extending these arguments to the Si(100) vicinal surface, it was found that at zero temperature a transition from a double- to single-stepped surface occurs for miscut angles less than ~0.05°.[13] At finite temperature a model Hamiltonian was used to study ledge roughening; at 500 K the transition angle showed a fortyfold increase to ~2°.[13]

In this Letter we report atomistic simulation calculation of energies of single- and double-layer ledges with semi-infinite stripe terraces on Si(100). Using the interatomic potential function proposed by Stillinger and Weber[14] (SW), we find that at sufficiently large ledge separations all three stepped surfaces *SA*, *SB*, and *DB* have energies lower than the 2×1 surface. The energy lowering is due to stress relaxations associated with two types of interaction, a relatively short-range interaction generated by the force dipoles and varying as l^{-2}, and a longer-range interaction logarithmically dependent on l induced by the difference in stress component across the stress domains. Both the power-law and logarithmic variations are found in the present atomistic calculations, and the results serve to unify the different analyses of ledge interactions based on elasticity.[10,11] The simulation results also provide a new interpretation of existing STM data on the relative stability of single- and double-layer step ledges.[3,7,13] In contrast to Alerhand *et al.*,[13] we find that at zero temperature the single- to double-layer ledge transition occurs at a miscut angle of ~1°. By extending their model Hamiltonian to include corner effects, we show that at 500 K the transition occurs at 3°, or a threefold increase.

We consider a surface with semi-infinite stripe terraces as depicted schematically in Fig. 1. Following the structural models of Chadi,[9] the single- and double-stepped surfaces with the upper terrace dimerization axis perpendicular to the step ledge are denoted as *SA* and *DA*, respectively. The other two surfaces are denoted as *SB* and *DB*. Atoms on the *SA* ledge are fully bonded, while the lower-ledge atoms on *SB* and *DA* and the middle-ledge atoms on *DB* all have a dangling bond. The row of dangling bonds gives rise to rebonding by dimer formation with neighboring surface atoms. The rebonded dimers lie on the lower terrace in the case of *SB* and *DA*; in *DB*, they lie on a middle terrace. These structural features play an important role in determining the energetics; they also control the different initial states of stress in the ledge region. We take the dimen-

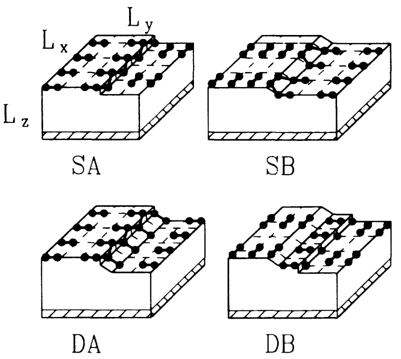

FIG. 1. Schematic diagrams of the simulation cell for various stepped surfaces. Hatched area represents four layers of atoms fixed in their ideal bulk configurations.

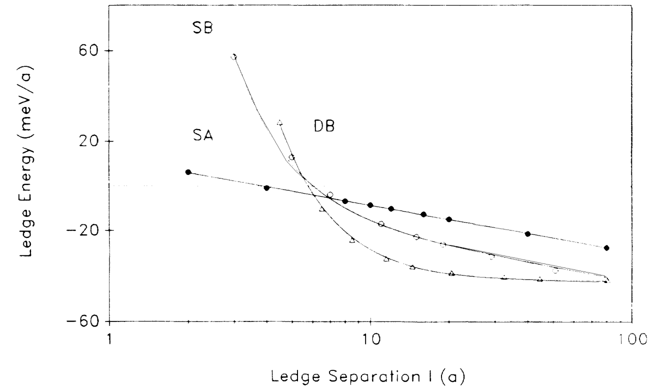

FIG. 2. Ledge energy vs ledge separation for various structures on the flat surface. Simulation results are shown as symbols; solid lines are fits discussed in the text. The unit of a is the surface lattice constant.

sion L_x to be four atomic layers, L_y treated as variable, and L_z large enough so that bulk behavior is obtained away from the surface. This is realized by having a sufficient number of z layers in the calculation cell to allow atoms located immediately above the region of fixed atoms to have the correct bulk energy (within seven significant figures). With periodicity in the y direction, the ledge separation l is equal to $L_y/2$ and L_y for the flat and vicinal surfaces, respectively. We find that the depth of relaxation in the z direction increases with terrace size in the range of L_y from $6a$ to $102a$, from 22 to 134 layers. Over this range the number of atoms in the simulation increases from 492 to 54468.

The various stepped structures are relaxed through energy minimization by the conjugate gradient method. The ledge energy is defined as $\lambda = L_l^{-1}(E - N\varepsilon_b - L_xL_y\varepsilon_u)$, where E is the total energy, N the number of atoms in the simulation cell, ε_b the energy of a bulk atom (-4.33 eV), ε_u the energy of the uniform reconstructed 2×1 surface (1.33 eV/a^2), and L_l the length of the ledge ($2L_x$ for the flat surface and L_x for the vicinal surface). The surface lattice constant a is equal to 3.84 Å. The range of ledge separation spans from 10 to 200 Å. As shown in Fig. 2 the ledge energy decreases with increasing l in all cases. The decrease over the range studied is comparable to thermal energy k_BT per ledge atom at room temperature. Since λ is defined with respect to the flat surface, we observe that all the stepped structures have lower energies than the 2×1 surface beyond a ledge separation of $\sim 7a$. This crossover occurs first for *SA*, then *DB* and *SB*. We note that at small l, *SA* is the lowest in energy among the three structures, and at large l, *SB* is the lowest. Although not shown in Fig. 2, we have also studied the *DA* ledge. While its behavior is similar to *DB*, the energy associated with broken bonds is so high (≥ 160 meV/a) that λ is positive over the entire range of ledge separation studied.

In the case of *SA* we see that over the two decades of l values, the simulation results show a logarithmic variation. Marchenko has given a general argument based on elasticity theory showing that when two phases of different surface stress exist, the deformation (strain-field) energy varies logarithmically with the dimension separating the two phases.[11] By fitting our data by the form $\lambda_0 - \lambda_\sigma \ln(l/\pi a)$ (see Table I), we obtain $\lambda_\sigma = 9.07$ meV/a, which is in reasonable agreement with the value of 11.5 meV/a obtained using electronic-structure calculation with tight-binding approximation.[12] In the case of *DB*, we can observe a relatively strong repulsive ledge-ledge interaction at small ledge separations. Fitting the

TABLE I. Excess ledge energies (meV/a).

Type	λ_0	λ_σ	λ_d
Stepped surface			
SA	1.88 ± 0.19	-9.07 ± 0.11	⋯
SB	-11.16 ± 0.67	-9.07	626.52 ± 17
DA	160.68 ± 0.15	⋯	524.75 ± 11
DB	-42.44 ± 0.36	⋯	1417.30 ± 19
Vicinal surface			
SA+*SB*	-9.29 ± 0.84	-9.32 ± 0.18	727.81 ± 65
DA	160.64 ± 0.07	⋯	602.86 ± 2.33
DB	-42.43 ± 0.67	⋯	1271.70 ± 21

data by an inverse power law we obtain $\alpha = 2.17 \pm 0.04$, which is close to the theoretical value of 2 for the force-dipole interaction between ledges as analyzed by linear elasticity.[10] We refit our data of *DB* (also data of *DA*) by the form $\lambda_0 + \lambda_d (a/l)^2$. For *SB*, we note the presence of force-dipole interaction in addition to stress-domain interaction. Thus we fit the data by

$$\lambda = \lambda_0 - \lambda_\sigma \ln(l/\pi a) + \lambda_d (a/l)^2 . \qquad (1)$$

The value of λ_σ in this case is taken to be the same as in *SA* because of the purely logarithmic variation in the latter. Examining the atomic configuration of all the ledges we conclude that the force dipole is induced by ledge rebonding.

Thus far we have only discussed the ledge energies on the flat surface. We present next results calculated for the vicinal surface. In Fig. 3, both stress-domain and force-dipole interactions are observed on the single-stepped vicinal surface (SL) composed of alternating *SA* and *SB* ledges, and only force-dipole interaction is observed on the double-stepped vicinal surfaces (DL). Therefore, qualitatively the behavior on a vicinal surface is the same as that on a flat surface. We then fit the SL data by Eq. (1) and the DL data by a l^{-2} variation (see Table I). The following points of consistency should be noted. The values of λ_0(DL) on flat and vicinal surfaces are identical to within the estimated uncertainty. λ_0(SL) on the vicinal surface is the same as the addition of λ_0 for *SA* and *SB* ledges on the flat surface. The coefficient of the stress-domain interaction λ_σ is also identical on flat and vicinal surfaces. In contrast, the coefficient for the dipole interaction λ_d is different for the two surfaces. Since the moments created at the ledges on flat and vicinal surfaces have opposite signs, this can result in different λ_d values.

In Fig. 3 a crossover is seen between the ledge energies of DL vicinal surfaces composed of *DB* ledges, and those of SL. The miscut angle θ is related to l by $\tan\theta = (\sqrt{8}l/a)^{-1}$. At angles above 1°, DL is seen to have the lower energy, the inequality being reversed at angles below 1°. This crossover behavior is consistent with experimental observations[2-8] of single-stepped surfaces at low miscut angles and double-stepped surfaces at high miscut angles. Recently Alerhand *et al.*[13] have indicated that at zero temperature the crossover will occur at a much lower angle of 0.05°, which corresponds to the single-layer terrace size l of about $400a$. This result is based on the assumptions that the force-dipole-interaction effects can be ignored and that the value of the ledge formation energy λ_0 can be taken from an electronic-structure calculation.[9] The coefficient of the stress-domain interaction λ_σ in their calculation is comparable to ours. In arriving at our result of 1° we find $\Delta\lambda_0 = \lambda_0(\mathrm{SL}) - \lambda_0(\mathrm{DL}) = 33$ meV/a, which is less than one-third of the value of 110 meV/a obtained on the basis of Chadi's calculation.[9] In that calculation, thin slabs of about twelve layers with 5.4° miscut angle were used. In our work we have found a significant dependence of λ_0 on slab thickness. In going from a twelve-layer-thick slab to a slab thick enough for energy convergence ($\sim$40 layers) we found λ_0 (using the SW potential) to decrease by a factor of $\sim$2. Thus the effect of slab thickness would lower the 110-meV/a estimate toward our value. Furthermore, we found that the contributions from the elastic interactions to the ledge energy of a vicinal surface with such values of miscut angle are appreciable. At 5.4°, we obtain $\Delta\lambda = 21.74$ meV/a.

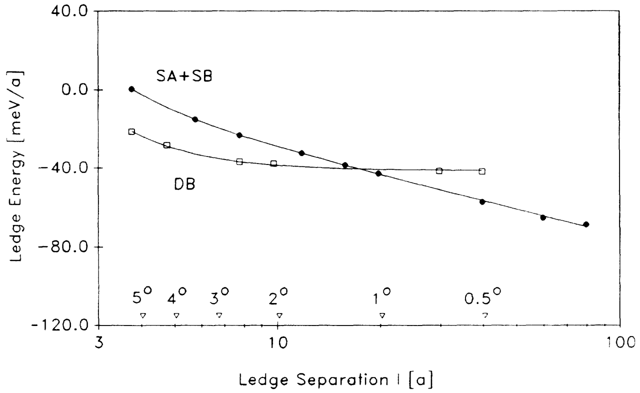

FIG. 3. Ledge energy vs single-layer surface terrace size l for various vicinal surfaces. The scale of the miscut angle is drawn at the bottom of the figure. Simulation results are shown as symbols; solid lines are fits discussed in the text.

We now consider finite-temperature effects on the crossover between vicinal single- and double-stepped surfaces. In the case of *SA*, both rebonded and nonbonded *SB* ledges can form as a result of thermal roughening. The former will give rise to a dipole-dipole interaction ($\Delta\varepsilon \sim 60$ meV/a) and the latter to the presence of dangling bonds ($\Delta\varepsilon \sim 400$ meV/a). In the case of *SB*, the formation of *SA* ledges (separated by $2a$) requires an energy of about 6.3 meV/a. In the case of *DB*, the formation of *DA* also induces dangling bonds, while the formation of *SA* and *SB* will require less energy but more ledges will be created. As a result, the only low-energy excitation is the roughening of *SB*. We generalize the fluctuation model proposed by Alerhand *et al.*[13] by including the energy cost of the creation of corners in a jagged ledge. Our Hamiltonian has the form

$$H = \sum_i [\lambda_\perp |h_i - h_{i-1}| + \kappa h_i^2 + 2\varepsilon_c (1 - \delta_{h_i, h_{i-1}})] , \qquad (2)$$

where h_i represents the fluctuations of the ith segment of the ledge front in units of the dimer length ($2a$) relative to its position at zero temperature. $\lambda_\perp$ is the energy cost per unit length of a ledge created in the perpendicular direction ($= 6.3$ meV/a). The spring constant is $\kappa = \lambda_\sigma / 8(l/a)^2 + 3\lambda_d / 16(l/a)^4$. The first term has its origin from the strain energy associated with the stress-domain interaction and the second term is associated with the force-dipole interaction, as described in Eq. (1). (In the

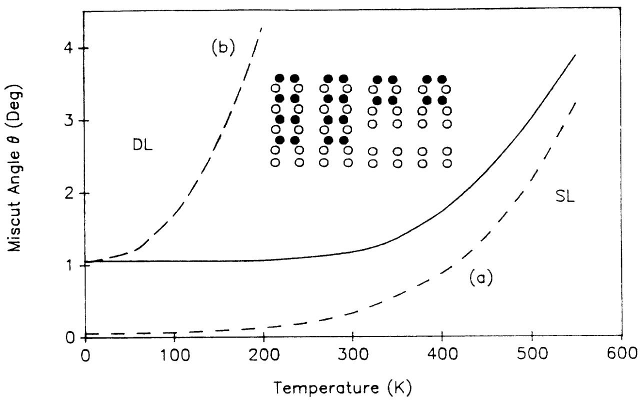

FIG. 4. Phase diagram of the vicinal Si(100) stepped surface. Dashed line *a* represents the result obtained by repeating the calculation of Alerhand *et al.* (Ref. 13) but excluding π^2 in the spring constant κ. Dashed line *b* represents the calculated phase boundary without the inclusion of corner energy. Inset: The atomic configuration with ledge corners. Solid and open circles represent atoms on the top and second layers, respectively.

spring constant κ in Ref. 13 the factor π^2 should not appear.) ε_c is the creation energy of a corner in a jagged ledge. An energy calculation using the SW interatomic potential yields $\varepsilon_c = 54$ meV.[15] The corresponding partition function Z_H can be calculated using the transfer-matrix method with the matrix taking the form

$$\langle h | e^{-\kappa h^2/2k_BT} e^{-\lambda_\perp |h-h'|/k_BT} \times e^{-2\varepsilon_c[1-\delta(h-h')]/k_BT} e^{-\kappa h'^2/2k_BT} | h' \rangle .$$

The phase boundary is then given by

$$\Delta\lambda_0 - k_BT \ln Z_H - 2\lambda_\sigma \ln(l/\pi a) + [\lambda_d(SB) - \lambda_d(DB)](a/2l)^2 = 0 . \quad (3)$$

Figure 4 shows the calculated phase diagram. From 400 to 500 K, the crossover angle has the value from 2.5° to 3°. The averaged fluctuation size $\langle h^2 \rangle^{1/2}$ on a surface with a 0.5° miscut angle is calculated to be $50a$ and $60a$ at 400 and 500 K, respectively, which agrees with experimental observation.[7]

In summary, we have demonstrated the important role of surface stress relaxation in determining the energies of single- and double-stepped Si(100) surfaces. Two types of ledge-ledge interactions are involved, a stress-domain interaction due to surface-stress anisotropy and a force-dipole interaction due to ledge rebonding, each having its own characteristic variation with ledge separation. The simulation results also show[15] that the mechanism of energy lowering on these stepped surfaces is indeed the stress-relaxation process first pointed out by Marchenko[10,11] and later elaborated upon by Alerhand *et al.*[12] Our results provide a consistent treatment of the competing effects between local bonding and elastic interactions regarding the engergetics. This consistency is shown to be important in the prediction of relative stability of single-layer and double-layer ledges. While strain-field effects derived from continuum theory appear to manifest on an essentially atomic level, proper inputs from microscopic considerations are crucial for a quantitative description of the phase diagram.

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[1] See, for example, H. Kroemer, in *Heteroepitaxy on Silicon,* edited by J. C. C. Fan and J. M. Poate, MRS Symposia Proceedings No. 67 (Materials Research Society, Pittsburgh, 1986).

[2] D. Saloner, J. A. Martin, M. C. Tringides, D. E. Savage, C. E. Aumann, and M. G. Lagally, J. Appl. Phys. **61**, 2884 (1987).

[3] P. E. Wierenga, J. A. Kubby , and J. E. Griffith, Phys. Rev. Lett. **59**, 2169 (1987).

[4] C. E. Aumann, D. E. Savage, R. Kariotis, and M. G. Lagally, J. Vac. Sci. Technol. A **6**, 1964 (1988).

[5] A. J. Hoeven, J. M. Lenssinck, D. Dijkkamp, E. J. van Loenen, and J. Dieleman, Phys. Rev. Lett. **63**, 1830 (1989).

[6] M. Mundschau, E. Bauer, and W. Telieps, Philos. Mag. A **61**, 257 (1990).

[7] R. J. Hamers, U. K. Köhler, and J. E. Demuth, J. Vac. Sci. Technol. A **8**, 195 (1990).

[8] M. G. Lagally, Y. W. Mo, R. Kariotis, B. S. Swartzentruber, and M. B. Webb, in *Kinetics of Ordering and Growth at Surfaces* (Plenum, New York, 1990).

[9] D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).

[10] V. I. Marchenko and A. Ya. Parshin, Zh. Eksp. Teor. Fiz. **79**, 2576 (1980) [Sov. Phys. JETP **52**, 129 (1980)].

[11] V. I. Marchenko, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 397 (1981) [JETP Lett. **33**, 381 (1981)].

[12] O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).

[13] O. L. Alerhand, A. N. Berker, J. D. Joannopoulos, D. Vanderbilt, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **64**, 2406 (1990).

[14] F. Stillinger and T. Weber, Phys. Rev. B **31**, 5262 (1985).

[15] T. W. Poon, Ph.D. thesis, MIT, 1990 (unpublished); T. W. Poon, S. Yip, P. S. Ho, and F. F. Abraham (to be published).