Unified description of silicon (111) surface transitions

D. Haneman*
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304
(Received 3 August 1981)

It is assumed that a strained strip of about 25 Å width occurs at the bases of steps on Si(111) surfaces. Evidence supporting this is summarized and quantitative estimates for the strain energy and strain at the edge of the strip yield approximately 0.32 eV and 0.1, respectively, which are sufficient to inhibit reconstruction. The various structural transitions that occur on Si(111) are then accounted for in a natural and unified way.

The (111) surface of silicon differs from the other low-index faces in that at least three different clean-surface structures appear to be observable at room temperature. Upon cleavage, the (2×1) low-energy electron diffraction (LEED) pattern appears, which is interpreted to indicate a buckling of the surface,[1] as supported by various experimental[2,3] and theoretical evidence.[4,5] This structure is a metastable one, created by the rupture forces that caused the cleavage. These forces also determine the preferred direction[6,7] of the (2×1) buckling on the otherwise threefold symmetric substrate.

Annealing of the cleaved surface in high vacuum (15 min) to temperatures ranging from about 210° to 425 °C depending on step density,[8] causes an irreversible transition to a surface showing a (7×7) LEED pattern. The atomic arrangement on this surface remains under discussion—the most recent models feature islands[9,10] or paired atom groups.[11]

If the (7×7) surface, which is stable at room temperature, is heated to a temperature near 870 °C, the seventh order [referred to a (1×1) cell] LEED diffraction beams disappear in a fairly continuous manner leaving only integral spots, a (1×1) pattern, but with an increased background.[12] This pattern returns to a (7×7) one if the specimen is slowly cooled through the transition temperature region, but quench cooling to room temperature results in maintenance of a (1×1) pattern.

When a (111) surface is subjected to laser annealing (after etching or mild ion bombardment), a (1×1) pattern is also observed at room temperature.[13,14] (Typical laser pulses[13] are about 2 J cm^{-2}, 15 $\times$ 10^{-9} s pulse width, 4—5 mm diameter.) The nature of this surface is currently under discussion but a good LEED dynamical analysis fit to experiment has been obtained from a (1×1) model featuring some surface contraction.[13] Such laser annealed surfaces are known to have a ripple topography[15,16] but a simple interpretation is to regard them as quench cooled surfaces, and hence, the LEED pattern is consistent with that obtained by quench cooling a normally heated surface.

The purpose of this work is to relate the various transitions and the (7×7) and (1×1) structures. We do this by proposing that surface strain acts as an inhibitor of surface reconstructions. We first show that this hypothesis is plausible, and then show how its application accounts for the above otherwise diverse phenomena.

A surface reconstructs to minimize its free energy. The lowering in free energy achieved by the reconstruction can be estimated theoretically[5,17–22] but not with great accuracy, due to difficulties with correlation effects and also entropy. The latter contribution has been estimated to be small.[17] The above referenced estimates of energy lowering due to reconstruction range from about 0.1 to 0.3 eV per unit cell.

We assume, and give supporting evidence below, that the occurrence of a step causes associated strain at its base region as illustrated in Fig. 1. We

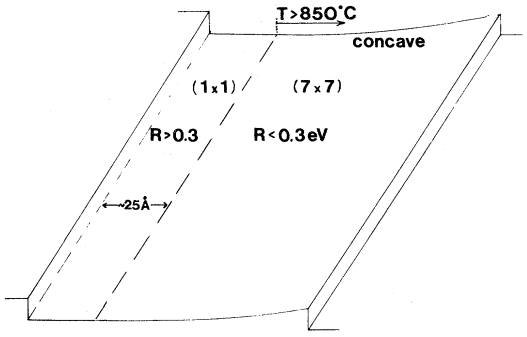

FIG. 1. Schematic diagram of strained region at base of atomic step, and surface reconstructions. R is reconstruction energy per unit cell.

shall show that this strain energy is of magnitude greater than 0.3 eV per unit cell and is thus sufficient to cause the surface structure to remain (1×1). This enables a consistent understanding to be obtained of the various phenomena, as follows

(i) The strain in the first layer, if induced by the proximity of the step will decay away from the step. Experimental evidence for the annealed (7×7) reconstruction on stepped surfaces has shown that only a (1×1) pattern is observable when the terrace width is reduced to about 25 Å.[23] This is consistent with the model if we assume the strain energy holds the surface to (1×1), but has reduced below the reconstruction-inhibiting value, at about 25 Å from the step. This assumption can be checked as follows.

(ii) Experiments on the (2×1) to (7×7) conversion temperature have shown[8] that it increases with step density in a manner describable by activation energy kinetics. From the data and expressions given it is possible to derive an expression for the structural conversion activation energy R as a function of distance l from the base of the step. We obtain from the data,[8] expressed in eV,

$$R=0.553\exp(-0.0223l)\ , \tag{1}$$

where l is measured in Å. This expression is plotted in Fig. 2. At 25 Å, R = 0.317 eV, i.e., approximately 0.3 eV, which is consistent with the energy estimates made above and is sufficient to inhibit reconstruction.

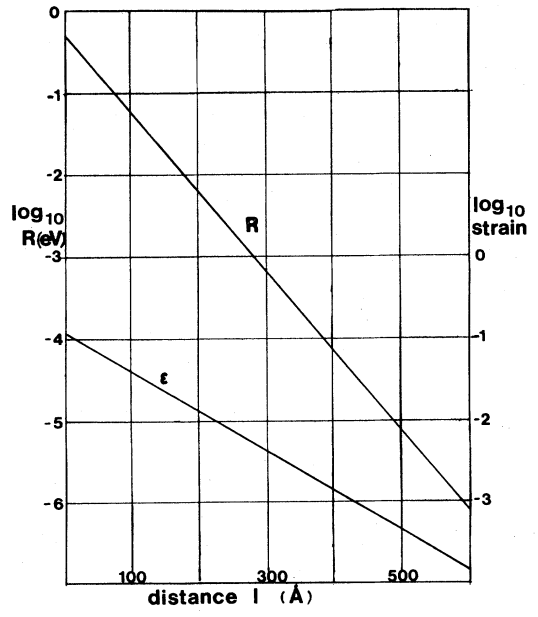

FIG. 2. Reconstruction energy R, plotted as function of distance l from base of step, from Eq. (1) using data of Ref. 8. Strain ϵ plotted as function of l using Eq. (2).

(iii) As a further quantitative check of the above concepts, we obtain an approximate expression for the strain energy. If ϵ is the strain, B is the bulk modulus, and V is the volume of a unit cell at the surface, taken as approximately 60 Å^3, then

$$E_s=B\epsilon(V\epsilon)=BV\epsilon^2 =37.5\epsilon^2 \text{ per unit cell}\ . \tag{2}$$

From this expression the strain corresponding to a strain energy of 0.1 eV is 0.052. Another estimate is obtainable from the force constants recently calculated for Si using self-consistent concepts.[24] The total force constant varies with phonon mode but taking an average value from the results[24] of about 15 (eV/Å^2), one obtains, for the work W for an atom movement Δx,

$$W=\tfrac{1}{2}K(\Delta x)^2\ . \tag{3}$$

For a strain of 0.052 in the bond length, $\Delta x = 0.122A$, giving W = 0.11 eV. Considering the crudity, this estimate compares well with the strain energy estimate of 0.1 eV above. Hence, we may use Eq. (2) adequately to relate reconstruction energy R to strain ϵ by equating E_s with R, which yields

$$\epsilon=0.1214\exp(-0.011\,15l)\ . \tag{4}$$

This expression is also plotted in Fig. 2. The strain at 25 Å from the step is 9×10^{-2}. Hence, one concludes that a strain of about 0.1, corresponding to a strain energy of 0.3 eV per unit cell, inhibits reconstruction for Si(111), the strain exceeding these values as the distance from the step edge reduces below 24 Å. Further support for the presence of a narrow ($\sim$25 Å) (1×1) strip on cleaved Si surfaces comes from measurements of decrease of contact potential differences with increase in step density. This was interpreted as due to the presence of an unconstructed strip along the step.[25]

If the (1×1) structure is that deduced by LEED analysis from laser annealed surfaces,[13] there are both simplifications and a testable consequence. The compression deduced for the LEED analyzed structure (25% of 1st-2nd layer spacing) provides a ready explanation for the strain. Furthermore, such a compression, which reduces with distance from the step edge, would cause the plateau to

bend with a concave curvature (viewed from above). Just such a curvature has already been deduced[26] from reflection electron microscopy measurements (Fig. 12 of Ref. 26). These measurements also deduced the presence of lattice strain around the steps from the similarity of contrast changes under different imaging conditions, for both steps and screw dislocations. Hence, these microscopy results are also fully consistent with the above model. (An attempt to estimate the strain quantitatively is made difficult by the breadth of contrast lines and asymmetry of step and dislocation strains.)

We are now able to provide a consistent description of the various structural changes on Si(111). The (2×1) structure is a metastable one initiated by rupture energy, as described above. Thermal annealing causes a transition to the equilibrium (7×7) structure at a temperature which is lower the further the region is from the strain around the base of a step. However, with 25 Å from the step, the strain energy exceeds 0.3 eV per unit cell and the strain-held (1×1) structure there cannot be converted. Above about 850 °C the (1×1) region is observed to spread outward from the base of the step across the plateau, and to contract back on lowering the temperature.[26] This transition is currently under discussion. If it is an order-disorder transition,[12] it is a reasonable occurrence on the above (or any) model. If it is a strain-induced (1×1) structure, it may be qualitatively accounted for by the increase in asymmetric lattice expansion forces at high temperatures. These reach the critical value for inhibiting reconstruction on the strained regions closest to the steps. This accounts for the (1×1) region being observed[26] to spread from the base of the step.

The (1×1) structure observed upon laser annealing can be regarded as the (1×1) structure which is observed above 850 °C, which is preserved at room-temperature by quench cooling. Such cooling is known to cause strain in materials, and hence, a qualitative explanation for the occurrence of the laser-annealed (1×1) structure is that it is a strained surface (as interpreted from LEED); the simplest view is that it is the (1×1) structure at the bases of steps.

Recently, measurements on various laser-annealed surfaces by Raman spectroscopy[27] have identified the presence of strain on such surfaces. Unfortunately, this method averages over a depth of 1000 Å so that the magnitude of the strain at the very surface cannot be accurately estimated. However, the presence of the strain is consistent with the model.

In conclusion, the concept of a strained region at the bases of steps on (111) surfaces, causing surface reconstructions to be inhibited, appears to be supported by a variety of data and is able to provide a unifying relationship between various structural transitions on Si(111). The different behavior of (100) surfaces, where the laser-annealed structure is the same as that produced by thermal annealing,[28] is then not unexpected, since the step structures are of different crystallography and there is no similar evidence for step-associated strain.

The author thanks his host institution for the opportunity to do this work.

---

*On leave from University New South Wales.

[1]D. Haneman, Phys. Rev. 121, 1093 (1961); A. Taloni and D. Haneman, Surf. Sci. 10, 215 (1968).
[2]R. Feder, W. Monch, and P. P. Auer, J. Phys. C 12, L179 (1979).
[3]R. U. Khokhar and D. Haneman, J. Appl. Phys. 43, 317 (1972); D. Haneman, J. W. T. Grant, and R. U. Khokhar, Surf. Sci. 13, 119 (1969).
[4]M. Schluter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 12, 4200 (1975).
[5]R. del Sole and D. J. Chadi, Phys. Rev. B 24, 7431 (1981).
[6]J. W. T. Ridgway and D. Haneman, Surf. Sci. 18, 441 (1969).
[7]M. Henzler, Surf. Sci. 36, 109 (1973).
[8]A. Freudenhammer, W. Monch, and P.P. Auer, J. Phys. C 13, 4407 (1980).
[9]M. J. Cardillo, Phys. Rev. B 23, 4279 (1981).
[10]E. G. McRae and C. W. Caldwell, Phys. Rev. Lett. 46 1632 (1981).
[11]D. J. Miller and D. Haneman, Surf. Sci. 104, L237 (1981) and unpublished.
[12]P. A. Bennett and M. Webb. Surf. Sci. 104, 74 (1981).
[13]D. M. Zehner, J. R. Noonan, H. L. Davis, and C. W. White, J. Vac. Sci. Technol. 18, 852 (1981).
[14]Y. J. Chabal, J. E. Rowe, and D. A. Zwemer, Phys. Rev. Lett. 46, 600 (1981).
[15]H. J. Leamy, G. A. Rozgonyi, and T. T. Sheng, Appl. Phys. Lett. 32, 539 (1978).
[16]D. Haneman and R. J. Nemanich (unpublished).

[17]D. L. Heron and D. Haneman, Surf. Sci. 21, 12 (1970).
[18]J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973); Surf. Sci. 74, 21 (1978).
[19]D. J. Chadi, Phys. Rev. Lett. 41, 1061 (1978).
[20]D. J. Miller and D. Haneman, J. Vac. Sci. Technol. 16, 1270 (1979).
[21]J. Ihm, M. L. Cohen, and D. J. Chadi, Phys. Rev. B 21, 4592 (1980).
[22]J. C. Phillips, Phys. Rev. Lett. 45, 905 (1980).
[23]J. E. Rowe, S. B. Christman, and H. Ibach, Phys. Rev. Lett. 34, 874 (1975).
[24]J. Ihm, M. T. Yin, and M. L. Cohen, Solid State Commun. 37, 491 (1981).
[25]S. Krueger and W. Monch, Surf. Sci. 99, 157 (1980).
[26]N. Osakabe, K. Yagi, and G. Honjo, Jpn. J. Appl. Phys. 19, L309 (1980).
[27]R. J. Nemanich and D. Haneman (unpublished).
[28]D. M. Zehner, C. W. White, and G. W. Ownby, Surf. Sci. 92, L67 (1980).