Biatomic Steps on (001) Silicon Surfaces

D. E. Aspnes and J. Ihm
Bell Communications Research, Red Bank, New Jersey 07701

(Received 11 August 1986)

The surprising tendency of clean (001) Si surfaces to become primitive upon annealing is explained by a π-bonded step reconstruction that lowers the relative enthalpy of reconstructed biatomic ($a_0/2$) steps on one particular fcc sublattice by 0.04 eV per step atom, and by correlation, which freezes out the step configurational entropy thereby suppressing the formation of other types of steps.

PACS numbers: 68.35.Bs, 68.35.Md

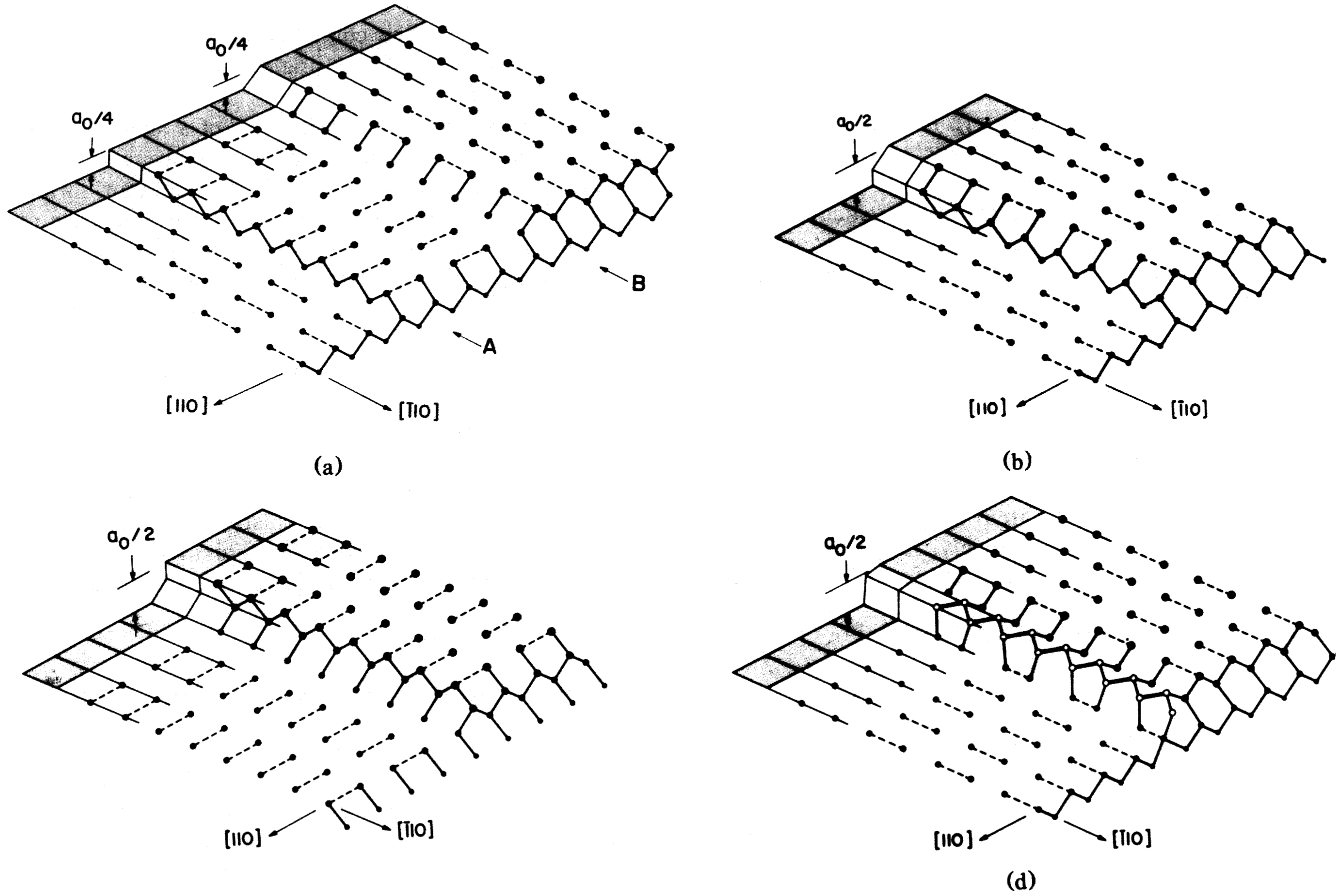
Atomically clean vicinal (001) Si surfaces tilted about [110] or [$\bar{1}$10] and annealed at high temperature for sufficient time are primitive, that is, consist entirely of atoms belonging to only one of the two inequivalent fcc sublattices of the diamond structure.[1] This surprising property is evident in the infrared vibrational spectra of hydrogen-covered surfaces,[1] which show only optical selection rules of hydrogen-silicon bonds of single-domain surfaces with dimer bonds parallel to the step edges, and is implied by low-energy electron diffraction (LEED) data,[2,3] which show biatomic ($a_0/2$) step heights and single-domain 2×1 LEED patterns consistent with surfaces terminated entirely by dimer bonds parallel to the step edges. More recently, the single-domain property has also been observed in reflection high-energy electron diffraction (RHEED) data[4] even on well oriented (001) surfaces.

This curious behavior has recently assumed new importance within the technologically relevant context of the heteroepitaxial growth of high-quality single-crystal GaAs on (001) Si substrates.[5-9] If present, monatomic ($a_0/4$) steps on the substrate would generate antiphase domains in the polar overlayer, that is, single-crystal regions terminated by boundaries where the atomic type changes from cationic to anionic (or vice versa) in a given (001) plane. Instead, cross-sectional transmission electron micrographs[10] of GaAs/Si heteroepitaxial interfaces reveal directly that elevation changes on properly prepared (001) Si substrates also occur via biatomic steps, which do not generate such domains. Various aspects of the GaAs/Si heteroepitaxial problem have recently been reviewed by Kroemer.[11]

A substantial amount of effort has been directed toward understanding the structure of the clean (001) Si surface,[12-18] but the reasons for the unusual stability of biatomic steps on one particular fcc sublattice have not been previously investigated. In this Letter, we show that this behavior is a natural consequence of two phenomena: a π-bonded step reconstruction that lowers the relative enthalpy of reconstructed biatomic steps on one sublattice by 0.04 eV per step atom, thereby favoring the formation of these steps, and correlation, which freezes out the step configurational entropy thereby suppressing the formation of other types of steps. Our model not only explains the remarkable stability of the observed primitive surface, but because the reconstruction is only possible for the sublattice with terrace dimer bonds oriented parallel to the steps, also naturally explains the infrared-absorption-spectroscopy, LEED, and RHEED data. Further, a generalization of our model to vicinal surfaces tilted about both [$\bar{1}$10] and [110] indicates why high-quality GaAs cannot be heteroepitaxially grown on vicinal (001) Si surfaces tilted about [100] or [010].[19]

Refer to Fig. 1(a), which shows the two distinct monatomic step structures A and B (in the notation of Kroemer[11]) that can accommodate a macroscopic slope on a (001) surface tilted about [$\bar{1}$10]. As a visualization aid we show only the atoms of the outermost surface planes drawn in their unrelaxed bulk positions. The equivalent geometric planes are shown shaded. The dimer bonds formed on the surface in its natural clean state are indicated by the dashed lines distributed in 2×1 (lower and upper terraces) and 1×2 (middle terrace) patterns. The orientation of these dimer bonds relative to the step edges is determined by the bonding configurations of the corresponding terminating fcc sublattices. In actuality the dimers may be asymmetric[13,14,16,17] and the terrace row spacings somewhat contracted,[3] but these complications are of no consequence in the following development. It is clear that A and B steps must alternate, and that nonprimitive surfaces are characterized by any and all of the following: monatomic elevation changes, rotation of dimer bonds by 90° on successive terraces, and the coexistence of 2×1 and 1×2 terrace reconstruction patterns.

Figures 1(b) and 1(c) show the simplest step structures by which macroscopic slopes can be accommodated by primitive surfaces. It is immediately evident that these configurations can be generated from Fig. 1(a) by simply filling in the appropriate terraces. Consequently, no significant driving force exists to discriminate among nonprimitive monatomic or these particular biatomic step configurations; in thermal equilibrium all should occur, in contrast to experiment. Accordingly, the solution to the stability problem must involve a more radical configuration.



(a)

(b)

(d)

FIG. 1. (a) Diagram of a vicinal (001) Si surface tilted about [1̄10], with the macroscopic inclination accommodated by monatomic steps. Parts of four (001) planes can be seen, with the three uppermost keyed to the shaded flats in the rear of the figure by means of the light solid lines. For simplicity, only the outermost atoms are shown. Atoms belonging to a given (001) plane are shown of the same size, with sizes increasing in the [001] direction. Dimer bonds are represented by dashed lines in the 2×1 pattern for the lowest and highest terraces and in the 1×2 pattern for the middle terrace. (b),(c) As (a), but for the simple biatomic step configurations generating the 2×1 and 1×2 primitive surfaces, respectively, corresponding to each of the two sublattices of the diamond structure. (d) As (b), but the π-bonded step reconstruction.

Recalling that π bonding describes the lowest-energy configuration of the 2×1 reconstruction of the clean (111) Si surface,[20] we investigate the possibility that it may be a factor here. Figure 1(d) shows that it is. Note that the π-bonded step reconstruction can be generated from the biatomic configuration of Fig. 1(b) by simply moving the zigzag bonding pattern from the vertical to the sloped riser. The atoms in the upper row of the π-bonded chain essentially remain in their bulk positions, while the atoms in the lower row are supported by what ordinarily would be dangling orbitals of dimerized terrace atoms. Because the modifications required to generate Fig. 1(d) from Fig. 1(b) involve only bond topology and not mass transport, we arrive at the important conclusion that kinetic barriers to the formation of π-bonded steps must be essentially nonexistent. Thus the stability problem itself can be addressed by equilibrium thermodynamics. We also note that the isolation of two adjacent rows of Si atoms, the key feature that allows π bonding to develop, is only possible for the terrace configuration of Fig. 1(b). Therefore, the π-bonded step reconstruction is intimately connected to the 2×1 pattern, as opposed to the 1×2 terrace pattern, in agreement with experiment.

To investigate this reconstruction quantitatively, we performed total-energy-minimization calculations for the configurations indicated in Figs. 1(a)-1(d). The tight-binding method of Chadi[13] was used with five atomic orbitals (excited s orbital inclusive) in the basis set. The relative accuracy of the present scheme, 0.01 eV per step atom, was carefully crosschecked against pseudopotential calculations previously reported for the flat (001) Si surface.[17] The results show that the formation of the π-bonded chain of Fig. 1(d) lowers the total energy per step atom by 0.04 eV relative to the geometry of Fig. 1(b) or, equivalently, to that of Figs. 1(a) or

1(c). Thus the formation of π-bonded biatomic steps is energetically favored.

However, an equally important characteristic of primitive surfaces is the absence of monatomic steps, a feature that does not necessarily follow from simple energy considerations. To understand this aspect we must examine the system thermodynamics in detail. We shall indicate here only the essential elements of the calculation; full details will be published elsewhere. We consider a vicinal (001) surface of length $L_{y'}$ along $[\bar{1}10]$ and projected length $L_{x'}$ along [110], generated by a small rotation about $[\bar{1}10]$. There are $N_{x'}=2^{1/2}L_{x'}/a_0$ atomic rows along $x'=[110]$ and $N_{y'}=2^{1/2}L_{y'}/a_0$ atomic columns along $y'=[\bar{1}10]$. Since both $L_{x'}$ and $L_{y'}$ can be considered macroscopic distances, $N_{x'}$ and $N_{y'}$ are both large numbers. If the tilt angle is θ, then any column contains on the average $N_z=2L_{x'}\tan(\theta)/a_0$ biatomic steps. If we assume enthalpies per step atom of h_A, h_B, and h_π for A, B, and π-bonded steps, respectively, relative to that of a terrace atom, and n_A $(=n_B)$ and n_π steps of each type, where $n_A+n_\pi=N_z$, the contribution of the steps to the total enthalpy H of a single isolated column is $H=(h_A+h_B)n_A+2h_\pi n_\pi$.

The total free energy $G=H-TS$ of a single isolated column can now be calculated by evaluating the total number of complexions N of the column, where $S=k\ln(N)$.[21] However, this is only an intermediate result, because steps do not occur randomly on different columns but typically divide the surface into terraces that retain their individual identities for finite distances along the steps. This column-to-column correlation can be described in an elementary way by assuming that steps either continue unchanged across columns or that kinks, the elementary excitations of a stepped surface,[22] deflect steps by one length unit $2^{1/2}a_0$ along x' between any two columns. On the assumption of a mean enthalpy h_κ per kink and a random distribution of M kinks over the surface, it is straightforward to show that the total free energy of the system is given in this model by

$$G=N_{y'}N_z\Big((h_A+h_B)(1-\xi)+2h_\pi\xi+\sigma h_\kappa+kT\{\sigma\ln\sigma+(1-\sigma)\ln(1-\sigma)-\sigma\ln 2 + [\xi\ln\xi+(1-\xi)\ln(1-\xi)+\ln(N_z/N_{x'})-1+N_z/N_{x'}]/N_{y'}\}\Big),$$

where $\sigma=M/N_{y'}N_z$ is the relative fraction of kink sites and $\xi=n_\pi/N_z$ is the relative fraction of biatomic elevation changes involving π-bonded steps. The first and second terms in large parentheses are the configurational entropies of the kinks and steps, respectively.

The reason for the suppression of monatomic (and non-π-bonded biatomic) steps is now clear. Correlation, which manifests itself as the denominator $N_{y'}$ in the step configurational entropy, acts to freeze this term out of the free energy. G is then minimized for $\xi=1$ or 0 according to whether h_A+h_B is greater to, or less than, $2h\pi$. Since the total-energy-minimization calculations show that the smaller enthalpy is associated with π bonding, the result $\xi=1$ follows.

From a more general point of view, $L_{y'}$ is not necessarily the full width of the surface but actually a correlation length that represents the distance over which a given terrace retains its identity. An important case where $L_{y'}$ is less than the sample width occurs for (001) surfaces tilted toward both [110] and $[\bar{1}10]$. Because $L_{y'}$ cannot exceed the maximum average spacing between steps, for sufficient bidirectional tilting the step-configurational-entropy term cannot be neglected. Then the free energy is minimized for ξ values other than 0 or 1; that is, a finite density of monatomic steps must occur. Because π-bonded steps can also form across the short dimension of terraces if monatomic steps are allowed, their contribution to the enthalpy also acts to increase the probability of formation of monatomic steps. In the limit of equal tilt angles about [110] and $[\bar{1}10]$ no distinction between 2×1 and 1×2 regions remains and the surface cannot be primitive.

Some remarks concerning the implications of these results to heteroepitaxial growth can now be made. Because primitive surfaces cannot be realized for vicinal surfaces generated by small rotations about [100] or [010], to the extend that antisite domains are important it should not be possible to grow good polar material on such surfaces. This appears to be in agreement with recent experiments.[19] Measurements on (001) vicinal surfaces unequally rotated about both $[\bar{1}10]$ and [110] to determine the relative importance of the step-configurational-entropy term would be of considerable interest, as it has been proposed that steps along both directions are necessary to suppress threading dislocations that arise from the lattice mismatch between Si and GaAs.[23]

Finally, although our results strictly pertain to clean-surface conditions that are quite different from those encountered in heteroepitaxy, we note that primitive (001) Si surfaces can be obtained in "reasonable," i.e., laboratory, times only at temperatures of the order of 1000 to 1100 °C, much higher than the 500–600 °C temperatures used for the heteroepitaxial growth of GaAs on Si. Consequently, the primary topological feature of the primitive surface, the biatomic step, should not be affected during the critical initial stages of heteroepitaxial growth even though the terrace atoms themselves appear to form chemical bonds with As.[24] Also, the tendency to form primitive (001) surfaces may not be a characteristic of Ge, a material for which π bonding is expected to be relatively unimportant.

We would like to express our appreciation to P. F.

Liao for encouragement during the initial phases of this project.

[1] Y. J. Chabal and K. Raghavachari, Phys. Rev. Lett. **53**, 282 (1984).

[2] M. Henzler and J. Clabes, Jpn. J. Appl. Phys., Suppl. 2, Pt. 2, 389 (1974).

[3] R. Kaplan, Surf. Sci. **93**, 145 (1980).

[4] T. Sakamoto and G. Hashiguchi, J. Appl. Phys. Jpn. **25**, L78 (1986).

[5] R. Fischer, T. Henderson, J. Klem, W. T. Masselink, W. Kopp, H. Morkoc, and C. W. Litton, Electron. Lett. **20**, 945 (1984).

[6] G. M. Metze, H. K. Choi, and B.-Y. Tsaur, Appl. Phys. Lett. **45**, 1107 (1984).

[7] T. Nonaka, M. Akiyama, Y. Kawarada, and K. Kaminishi, J. Appl. Phys. Jpn. **23**, L919 (1984).

[8] S. Sakai, T. Soga, M. Takeyasu, and M. Umeno, J. Appl. Phys. Jpn. **24**, L666 (1986).

[9] S.Sakai, T. Olga, M. Takeyasu, and M. Umeno, Appl. Phys. Lett. **48**, 413 (1986).

[10] N. Otsuka, C. Choi, R. Fischer, C. K. Peng, H. Morkoc, Y. Nakamura, and S. Nagakura, J. Vac. Sci. Technol. (to be published).

[11] H. Kroemer, in Proceedings of the Spring Meeting of the Materials Research Society, San Francisco, 1986 (to be published).

[12] J. A. Appelbaum and D. R. Hamann, Surf. Sci. **74**, 21 (1978).

[13] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).

[14] M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 2303 (1981).

[15] A. Redondo and W. A. Goddard, III, J. Vac. Sci. Technol. **21**, 344 (1982).

[16] L. Pauling and Z. S. Herman, Phys. Rev. B **28**, 6154 (1983).

[17] J. Ihm, D. H. Lee, J. D. Joannopoulos, and J. J. Xiong, Phys. Rev. Lett. **51**, 1872 (1983).

[18] J. E. Northrup, Phys. Rev. Lett. **54**, 815 (1985).

[19] S. Sakai, T. Soga, M. Takeyasu, and M. Umeno, in Ref. 11.

[20] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981).

[21] G. W. Castellan, *Physical Chemistry* (Addison-Wesley, Reading, MA, 1971), 2nd ed.

[22] W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. Roy. Soc. London, Ser. A **243**, 299 (1951).

[23] R. Fischer, D. Neuman, H. Zabel, H. Morkoc, C. Choi, and N. Otsuka, Appl. Phys. Lett. **48**, 1223 (1986).

[24] R. I. G. Uhrberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **56**, 520 (1986).

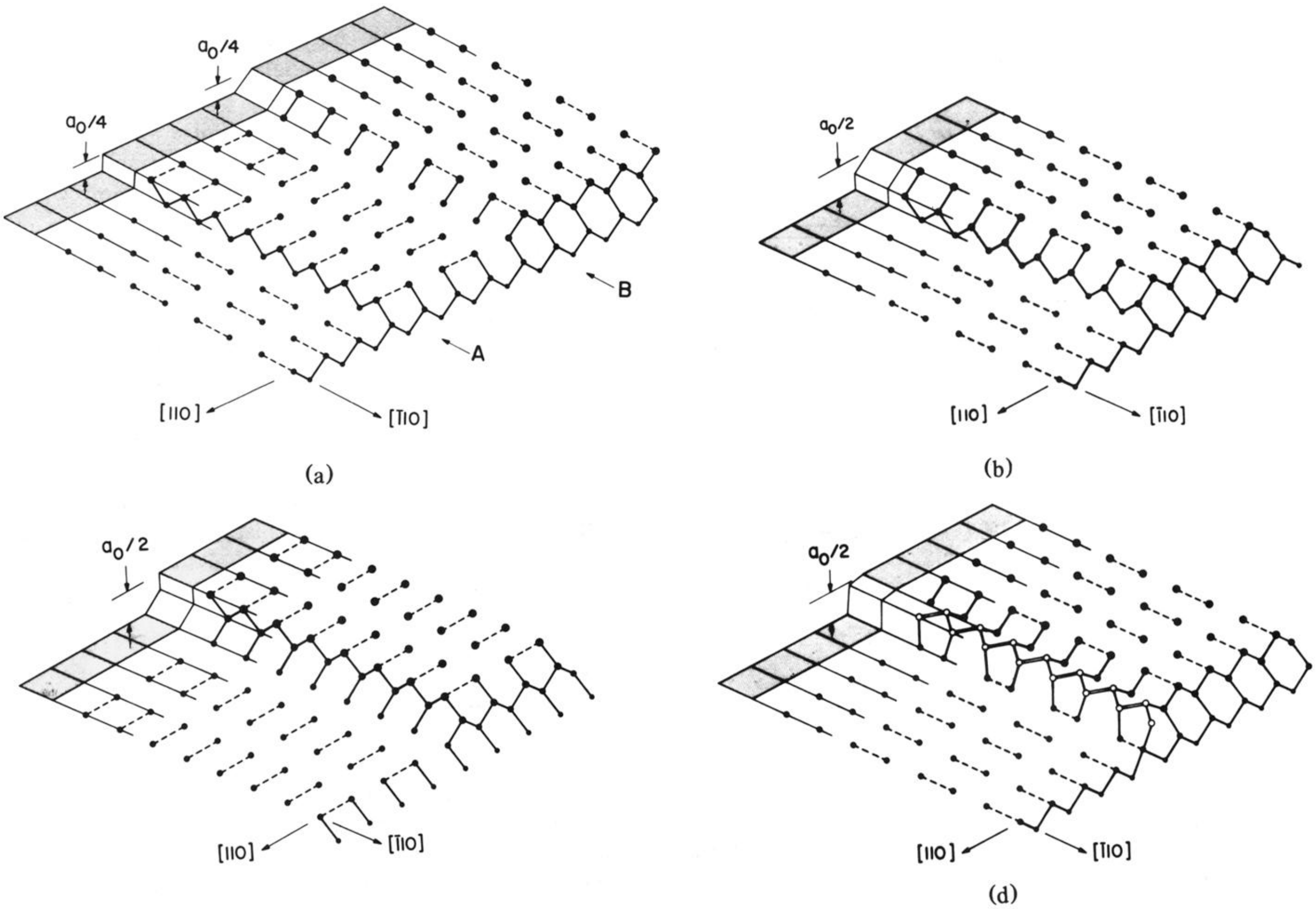


FIG. 1. (a) Diagram of a vicinal (001) Si surface tilted about [$\bar{1}$10], with the macroscopic inclination accommodated by monatomic steps. Parts of four (001) planes can be seen, with the three uppermost keyed to the shaded flats in the rear of the figure by means of the light solid lines. For simplicity, only the outermost atoms are shown. Atoms belonging to a given (001) plane are shown of the same size, with sizes increasing in the [001] direction. Dimer bonds are represented by dashed lines in the 2×1 pattern for the lowest and highest terraces and in the 1×2 pattern for the middle terrace. (b),(c) As (a), but for the simple biatomic step configurations generating the 2×1 and 1×2 primitive surfaces, respectively, corresponding to each of the two sublattices of the diamond structure. (d) As (b), but the π-bonded step reconstruction.