Evolution of Vicinal Si(001) from Double- to Single-Atomic-Height Steps with Temperature

J. J. de Miguel,[a] C. E. Aumann, R. Kariotis, and M. G. Lagally
University of Wisconsin, Madison, Wisconsin 53706

(Received 13 June 1991)

We have measured the evolution with temperature of the structure of vicinal Si(001) from double- to single-atomic-height steps using high-resolution low-energy electron diffraction. The observed temperature dependence is qualitatively explained with a model that describes this system in analogy with mixing equilibrium between two states, of which one is n-fold degenerate.

PACS numbers: 68.35.Bs

The Si(001) surface has been the object of intense interest. Aside from its obvious technological importance, it has also served as a fascinating model for covalently bonded materials. Si(001) reconstructs into a (2×1) structure consisting of rows of dimers parallel to [110] directions. Because of the underlying diamond lattice, terraces separated by one atomic level show orthogonal reconstructions [(1×2) and (2×1)]. The dimers are under strain, creating a multipolar strain field that is affected by the density of steps [1,2]. Surfaces miscut by a small amount toward the [110] direction exhibit single-atomic-height steps. Because of the orthogonal reconstructions these steps are alternately perpendicular and parallel to the dimer rows. The step terminating a terrace in which the dimer rows run perpendicular to the step (S_B) is quite rough, while the other (S_A) is smooth. The properties of these steps have been analyzed in great detail [3,4], and it has been possible to extract kink and terrace edge energies from measurements of their roughness [4].

Single-atomic-height steps form when the miscut angle is small, $\theta < 1°$. As the miscut angle is increased ($\theta > 2°$), the surface favors more and more the formation of double-atomic-height steps, D_B, with dimer rows perpendicular to the step. This phenomenon has been observed by a number of techniques [5–8]. The "transition" from single- to double-atomic-height steps has raised the question, "How and why does it occur?" Several contributions have addressed this issue. A calculation by Chadi [3], showing that D_B steps have lower energy than S_A and S_B, led to the suggestion that all Si(001) surfaces miscut toward [110] would, at equilibrium, consist of only double-atomic-height steps, with the presence of single-height steps being simply a kinetic limitation. Considerable evidence exists that this is not the case. Alerhand *et al.* [9] using Chadi's energies and a strain potential for Si(001) [1,2] formulated a theoretical model for a possible "phase transition" with vicinality. In this model, the equilibrium structure at low temperatures is double-height steps, which transform, in a first-order transition, to single-height steps at higher temperatures. For low enough vicinalities ($\theta \lesssim 2°$) the phase diagram predicts single-height steps to be stable at room temperature. Tong and Bennett [10], recognizing the temperature dependence in the theory, made the first measurements at different temperatures, 25 and 800 °C, for surfaces with vicinality in the range $0° \leq \theta \leq 8°$. Consistent with earlier work, they observed a gradual change in the fraction of the surface occupied by major [(2×1)] and minor [(1×2)] domains with increasing vicinality. They observed, however, no temperature dependence of the fractional occupation.

In this Letter, we report on high-resolution LEED measurements of the temperature evolution of the relative domain occupations of Si(001) surfaces of various vicinalities. In contrast to earlier work [10], we observe a gradual transition from double-height steps to single-height steps as the temperature is increased, primarily at temperatures above those used in Ref. [10]. These results are inconsistent with the existence of a first-order phase transition. We demonstrate that they can be explained in terms of a two-state-mixing equilibrium, without a need to invoke higher-order phase transitions.

The experiment consists of measuring the diffracted-beam intensities at appropriate diffraction conditions as a function of temperature. The instrument [11] allows very accurate measurements of intensities, including those of the components of the split fundamental reflections that are a hallmark of vicinal surfaces. These intensities, when measured at the appropriate diffraction conditions, reflect [6,12] the percentage of the surface covered by (2×1) and (1×2) domains. The use of the fundamental rather than the superlattice reflections [10] has two advantages: (1) Because of their greater intensity, it is possible to follow fundamental reflections to higher temperatures, and (2) the fundamental reflections measure area even as narrow as one dimer row, which would not appear in the superlattice reflections. Scanning tunneling microscopy (STM) scans show that such areas occur in surfaces with higher vicinalities [8]. The samples used in the study were extremely high-quality Si(001) wafers miscut toward [110] with very low azimuthal misorientation. Both the azimuthal and colatitude orientations have been independently checked with STM [4]. The samples were cleaned in the standard manner [8]. Clean samples display a LEED pattern with very sharp spots and low background. Measurements of the (0,0) beam are made at the out-of-phase conditions, a set of diffraction parameters at which the value of the perpendicular component of the momentum transfer, S_z, is such that waves diffracted from layers differing in height by a single atomic spacing destructively interfere. At these values of S_z, the profile of any fundamental beam should consist of two split peaks. We have previously shown that a third, central, component arises from two possible causes [6,12]. One is a multiple-scattering effect [6] that can be eliminated simply by an appropriate choice of the direction of the incident beam relative to the crystal, namely, the ⟨100⟩ direction; under these conditions the scattering factors of the unit area of (2×1) and (1×2) domains are equal. The second is the unequal areas of the (2×1) and (1×2) domains [12]. It is precisely this phenomenon that we wish to probe.

Most of the profiles of the (0,0) beam were measured at the first out-of-phase condition $S_z = 2.3$ Å^{-1}. The advantage of working at a low S_z is that thermal effects (Debye-Waller factor and thermal diffuse scattering) are optimally smallest here, allowing higher temperatures to be reached. There is negligible influence of either on profile shape or intensity at this S_z value. Figure 1 shows profiles of the (0,0) beam for various vicinalities measured at room temperature. The ratio of the integrated intensities in the central component and the sum of all components reflects the domain occupation asymmetry. If the central component is absent, occupations are equal. If the outer components were absent, the surface would consist of only one domain type, i.e., all double steps. The 0.3° sample shows negligible intensity in the central peak. As the vicinality is increased, the central component shows increasing intensity, reflecting increasing areal occupation difference. These measurements parallel the observed imbalance in the (2×1) and (1×2) superlattice intensities, which gave rise to the original (and correct) suggestions that the surface was progressing with increasing vicinality to one of primarily double steps (D_B), i.e., (2×1) terraces. Figure 2 shows similar measurements for the temperature dependence at one miscut. The intensity in the central component decreases with increasing temperature relative to that of the two outer components, clear evidence that the domain occupation ratio is changing. For the 4° miscut surface shown in

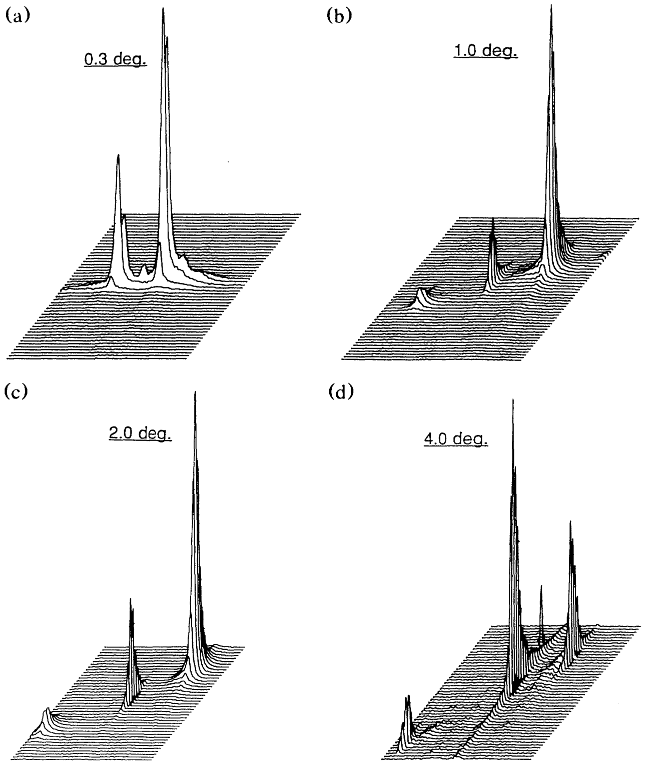

FIG. 1. Profiles of the (0,0) beam diffracted from Si(001) with several miscuts, measured at room temperature and at the first out-of-phase condition. The central peak indicates the presence of double-atomic-height steps through an asymmetry in occupation of (2×1) and (1×2) terraces.

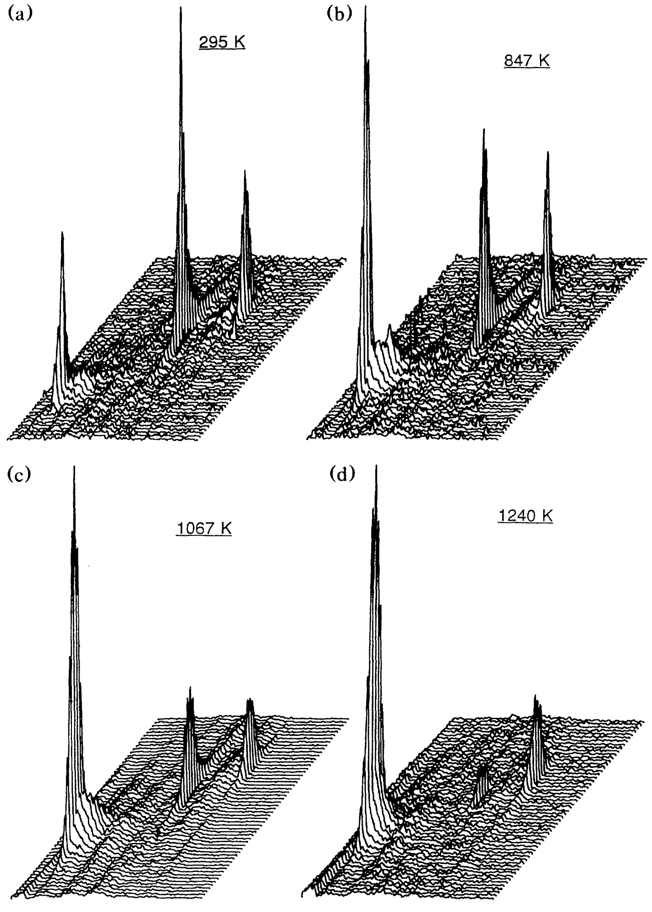

FIG. 2. Profiles at different temperatures of the (0,0) beam diffracted from Si(001) miscut by 4°. The decrease in the intensity of the central peak indicates a change in the relative occupation of the (2×1) and (1×2) domains. The difference in intensities of the two outer peaks is an instrumental effect; see text.

Fig. 2 there are essentially no double-height steps at 1240 K, but a mixture of singles and doubles at lower temperatures. Before data such as these can be interpreted quantitatively, they must first be corrected for the cut that the Ewald sphere makes with the reciprocal-lattice rod. If the diffraction conditions are chosen so that the central component is exactly at the out-of-phase conditions, the cut through the two outer components will generally not be. To correct for this, we have made measurements along each of the component rods and taken appropriate values at constant S_z [13]. Figure 3 shows the temperature dependence of the occupation for three vicinalities [14]. Figure 4 shows an occupation contour map for several vicinalities as a function of temperature.

How can these results be interpreted? The coexistence of singles and doubles over a wide temperature range is inconsistent with the existence of a first-order phase transformation. The data themselves do not preclude a higher-order phase transformation; however, one need not be invoked to explain the observations. We propose the following simple model. Consider a two-level system. The occupation of the two levels as a function of temperature is given by the Boltzmann factor. At low temperatures the lower level is occupied preferentially, while at high temperatures the occupations become equal. If now the upper level has an n-fold degeneracy, then at high temperatures the occupation is preferentially all in the upper level. Our system can analogously be thought of by recognizing that the "upper level" is the singles state S_B, which is n-fold degenerate, where n depends on the vicinality; the "lower level" is the doubles state D_B. If one now considers equilibrium between these states, there will be a concentration of singles and doubles that minimizes the free energy at any temperature. As the temperature is varied, this minimum shifts. This two-state equilibrium can be achieved by modifying the potential used by Alerhand *et al.* [9] through the inclusion of a D_B binding energy at the original S_A edge [15], now making two distinct states D_B and S_B that can mix. Such a model reproduces qualitatively the behavior we observe in the experiment, as shown in Fig. 4 (top). We know that the model with just the inclusion of a D_B energy is not precise in all details, as it neglects the cancellation of the strain fields through the formation of D_B steps [16–18]. This effect is nonlocal and influences the shape of the potential in a manner that depends on the configuration. The neglect of strain-field cancellation changes our conclusions only quantitatively, however. Once a more accurate description of the strain potential and its dependence on temperature is available, one can, in principle, extract the value of the D_B binding energy from our measurements.

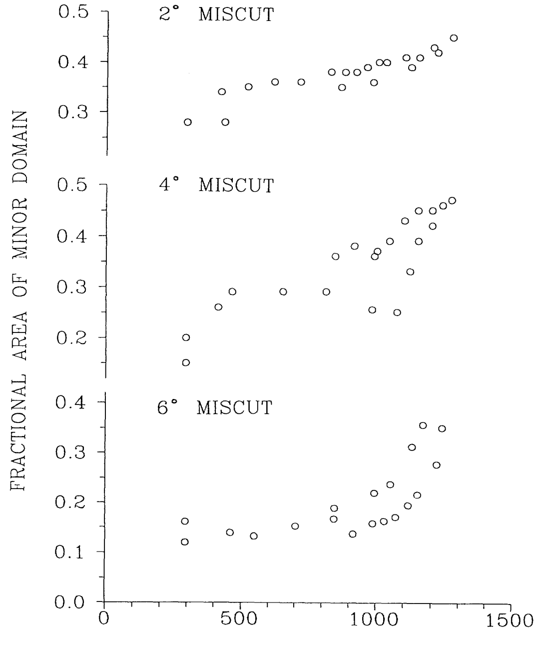

FIG. 3. Temperature evolution of the percentage occupation of the minority [(1×2)] domain in Si(001) for different miscut angles.

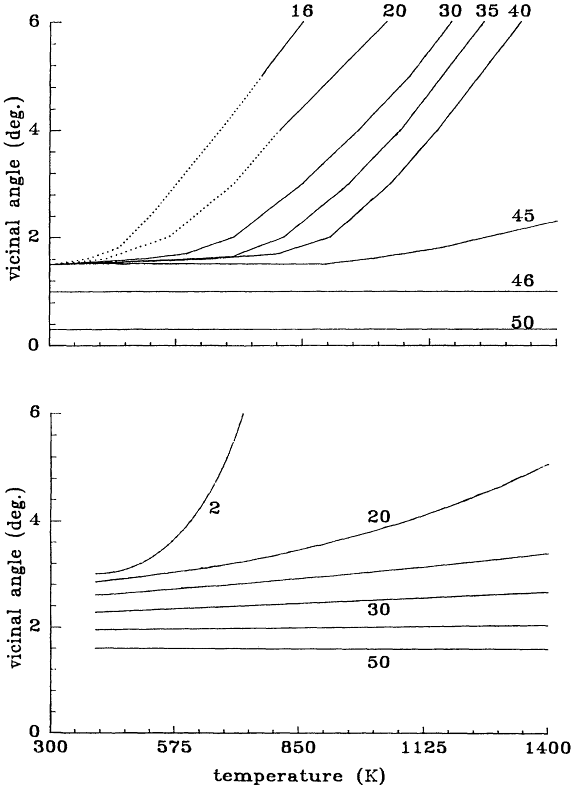

FIG. 4. Contour maps of minority domain [(1×2)] occupation for various vicinalities and temperatures. Each curve is the contour line for a specific percentage of occupation of minority domain. Top, experiment; bottom, model.

In conclusion, we have observed a temperature dependence of the relative occupation of domain types in vicinal Si(001), which, we believe, reflects the existence of a double-step binding energy. The system behaves as an equilibrium mixture of singles and doubles at every temperature, with equilibrium determined by the minimization of free energy. The system evolves with increasing temperature from the initial condition of primarily doubles (given sufficiently high vicinality) to primarily singles. We have proposed a model that qualitatively predicts the observed behavior. A quantitative determination of parameters controlling the temperature dependence of the step distributions must await a detailed description of the strain potential and accurate measurements of actual distributions of dimer-row lengths on each terrace, rather than just an occupation factor. Such work is in progress [18].

This research was supported by NSF, Solid State Chemistry Program, Grant No. DMR 89-15089. We thank D. E. Savage and M. B. Webb for useful discussions, M. Schacht for help with programming, and P. Wagner, Wacker Chemitronics, Burghausen, Germany, for supplying the Si wafers. J.J.M. thanks the Spanish Ministerio de Educación y Ciencia for fellowship support.

---

[a] Permanent address: Departamento de Física de la Materia Condensada, Universitá Autónoma, Cantoblanco, 28049 Madrid, Spain.

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

[2] F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. **61**, 2469 (1988).

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

[4] B. S. Swartzentruber, Y.-W. Mo, R. Kariotis, M. G. Lagally, and M. B. Webb, Phys. Rev. Lett. **65**, 1913 (1990).

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

[6] J. A. Martin, C. E. Aumann, D. E. Savage, M. C. Tringides, M. G. Lagally, W. Moritz, and F. Kretschmar, J. Vac. Sci. Technol. A **5**, 615 (1987).

[7] T. Nakayama, Y. Tanishiro, and K. Takayanagi, Jpn. J. Appl. Phys. **26**, L280 (1987).

[8] B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **7**, 2901 (1989).

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

[10] X. Tong and P. A. Bennett, Phys. Rev. Lett. **67**, 101 (1991).

[11] M. G. Lagally and J. A. Martin, Rev. Sci. Instrum. **54**, 1273 (1983).

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

[13] C. E. Aumann, J. J. de Miguel, and M. G. Lagally (to be published).

[14] STM and at higher-temperature LEEM show that fluctuations in step morphology occur as low as 300 °C. However, these will not affect domain occupation. In any case, diffraction measures a temporal and spatial average and is not sensitive to the instantaneous dynamics. Any possible preferential evaporation from one type of terrace would slow the measured change to singles, thus implying that the temperature-dependent change to singles shown in Fig. 3 represents a lower limit.

[15] M. G. Lagally, R. Kariotis, and M. B. Webb, Bull. Am. Phys. Soc. **36**, 910 (1991); (to be published).

[16] T. W. Poon, S. Yip, P. S. Ho, and F. F. Abraham, Phys. Rev. Lett. **65**, 2161 (1990).

[17] J. Pehlke and J. Tersoff, Phys. Rev. Lett. **67**, 1290 (1991).

[18] B. S. Swartzentruber, R. Kariotis, and M. B. Webb (to be published).