Phase Diagram of Vicinal Si(001) Surfaces

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(Received 22 May 1991)

Vicinal Si(001) surfaces are believed to undergo a phase transition between single and double atomic height steps as either temperature or angle of miscut is varied. Here we calculate the full temperature-angle phase diagram, which is found to be quite different than previously believed. In particular, there is a critical point above which there is no phase transition at all. The results appear to explain the rather continuous behavior seen in a variety of experiments.

PACS numbers: 68.35.Bs, 64.80.Gd, 68.35.Md

Surface steps are crucial in determining the growth and shape of crystals, and there has recently been intense interest in understanding the thermodynamics of steps, e.g., bunching, faceting, and step-height transitions [1,2]. In particular, steps on vicinal Si(001) surfaces miscut towards [110] exhibit a fascinating transition from single to double atomic height steps. Yet there is considerable controversy concerning the nature or even the existence of a phase transition for this surface [3,4]. Theoretical treatments have predicted a first-order phase transition with temperature and with angle of miscut from (001) [5-8]; yet experiments find only a continuous variation of all observable quantities [9-11].

Here, by calculating the full temperature-angle phase diagram, and including a more complete and accurate description of the fundamental thermal excitations of the system, we reconcile the predicted existence of a phase transition with the continuous behavior observed experimentally. We show that there is a thermodynamic critical point in the surface phase diagram, above which there is no phase transition with angle. If surface equilibration only occurs at temperatures above the critical point, then the phase transitions predicted theoretically should not be experimentally observable. In addition, the nature of the transitions is such that they should be far more difficult to identify in experiments than previously believed, even if they occur in an accessible temperature range.

It is well known from different experiments (see, e.g., references in [5]) that at small miscut angles the Si(001) surface consists of terraces of alternating 1×2 and 2×1 dimerization. These terraces are separated by single atomic height steps, which are denoted [12] S_A and S_B according to whether the dimerization on the upper terrace is perpendicular or parallel to the step edge, respectively. (On vicinal surfaces such steps must occur in S_A-S_B pairs, which we collectively call S steps.) At larger miscut angles double atomic height steps (denoted D_B) dominate [13,14], and the surface approaches a single domain structure, consisting of dimers parallel to the step edges (1×2 dimerization). Alerhand *et al.* [5] showed that this transition results from the elastic interaction between steps [15,16] which favors single height steps at large step-step separations (small angles of miscut), and double height steps at smaller separations.

The role of temperature has so far been included only as a contribution to the free energy of single height steps from meandering. Alerhand *et al.* [5], and later Poon *et al.* [8], calculated the free energy of meandering S_B steps on a single-height-stepped surface. (Meandering of the S_A is believed to be negligible.) They employed a one-dimensional model Hamiltonian including kink-energy terms and a harmonic potential (so that the S_B step energetically prefers a position in the middle between the two neighboring S_A steps).

Comparing the free energy of S steps with the energy of straight D_B steps, Refs. [5] and [8] concluded that there is a first-order phase transition with angle of miscut at any temperature, from a pure S phase to a pure D phase. However, experiments to date have not observed the abrupt transition predicted. Instead, only a continuous variation with angle [9,10] and temperature [11] has been observed.

There are two crucial elements missing in previous theoretical treatments of the surface at finite temperature. The first element is a correct identification of the zero-temperature structure. We recently showed that the transition from single to double steps with increasing angle is not abrupt; rather, it takes place through a (presumably infinite) sequence of phases consisting of distinct ordered mixtures of double (D) and pairs of single (S) height steps [17].

The second missing element is a comprehensive description of step meandering. The meandering of isolated S_B steps has already been treated in detail [5,8]. However, a double step may be viewed as a bound pair of single steps (S_A and S_B). At finite temperature, the S_B step of this pair may meander, breaking up the double step locally. This excitation has been proposed based on reflection high-energy electron diffraction experiments of Tong and Bennett [9], and seen in scanning tunneling microscopy experiments of Wierenga, Kubby, and Griffith [14]. And it is this excitation which blurs the distinction between single and double steps at high temperature, leading to a critical point in the phase diagram.

Before presenting results we briefly sketch our procedure. Rather than considering a single-step pair, we must consider at least two pairs of steps, in order to describe the tendency of the surface to form phases consisting of alternating single and double steps [17]. Such a set of two pairs is shown in Fig. 1. The spacing of these steps, in the absence of meandering, can be described by four parameters: l, l', d, and L. Here L is the overall periodicity, which is related to the surface miscut angle θ and surface lattice constant a by $L/a=\sqrt{2}/\tan\theta$; l and l' are the widths of the 2×1 terraces enclosed by two neighboring S_A and S_B steps; and d is the distance between the S_A steps. For meandering steps, we can so specify the spacing along any given atomic row in the [110] direction, i.e., perpendicular to the step.

The calculation of the interaction energy $v(l,l',d,L)$ is based on an elastic model [5,8,15,16,18], which has been widely and successfully employed to treat this surface. We include both the force monopole due to the anisotropy of the surface stress and the force dipole due to local rebonding at the S_B and D_B step edges. For the interaction parameters we take the values derived by Poon *et al.* [8]. However, one must bear in mind that these elastic parameter values were obtained by fitting to atomistic simulations which used an empirical model [19], so they may not be quantitatively accurate. Thus while the results here reliably describe the topology of the phase diagram, the actual temperatures and angles at which the transitions take place are rough estimates.

The geometry of a D_B step is essentially that of an S_A-S_B pair separated by about $1.5a$. In fact, by choosing the spacing to be $1.57a$, the long-range interaction field of the S_A-S_B pair becomes equivalent to that of a D_B step for the parameter values used here. Thus, with respect to the interaction with other steps, the D_B step may be treated simply as a bound pair of single steps. We need only add to the elastic model a short-ranged (contact) interaction between single steps to give the correct D_B step energy.

However, unlike earlier treatments, to describe the binding and unbinding of single-step pairs our elastic model must accurately reproduce the interaction of steps at atomic distances. We do this by broadening surface forces with a Lorentzian of width a, retaining the full complexity of the resulting cumbersome expressions. We have explicitly verified the accuracy of this treatment at all step separations.

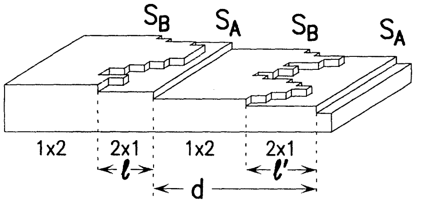

FIG. 1. Schematic drawing of a vicinal Si(001) surface with alternating straight S_A and meandering S_B single atomic height steps. The direction of dimerization is rotated by 90° on consecutive terraces. By 1×2 we denote terraces with Si dimer bonds parallel to the S_A step edge. When the S_B approaches the S_A step (separation $1.5a$) a local portion of D_B step is formed, as depicted in the left part of the figure.

The step meandering occurs in units of $2a$ parallel and perpendicular to the step edge, preserving the local atomistic structure of the steps [20]. The energy of a configuration of two meandering step pairs with total length $2Na$ parallel to the steps, and terrace sizes l_i and l'_i at the ith position along the step edge, is given by the Hamiltonian

$$H=\sum_{i=1}^{N}\left[\lambda_\perp|l_{i+1}-l_i|+2\epsilon_c(1-\delta_{l_{i+1},l_i})+\lambda_\perp|l'_{i+1}-l'_i|+2\epsilon_c(1-\delta_{l'_{i+1},l'_i})+2v(l_i,l'_i,d,L)\right]. \qquad (1)$$

Here $\lambda_\perp$ denotes the energy per length of the intervening S_A step, and ϵ_c is the corner energy of the kink. We use the values proposed in Ref. [8].

The free energy per 1×1 surface unit cell for a fixed separation d of the S_A steps is calculated in the usual way from the maximum eigenvalue $\lambda_{\max}$ of the transfer matrix:

$$f(T,\theta,d)=-\frac{k_BT}{2(L/a)}\ln\lambda_{\max}(T,\theta,d). \qquad (2)$$

Here k_B is Boltzmann's constant, and the factor of 2 in the denominator of the prefactor is due to the unit step of meandering being 2 times the 1×1 surface lattice constant. In equilibrium the free energy is minimized with respect to the S_A step separation,

$$f(T,\theta)=\min_d f(T,\theta,d). \qquad (3)$$

Note that, technically speaking, due to this minimization our model is effectively not one dimensional. It is the elastic interaction perpendicular to the step edges that leads to the existence of ordered structures of S and D steps, and to the corresponding phase transitions.

Because of the added complexity of treating finite temperature, we restrict ourselves to structures of up to two step pairs. The value of d that minimizes $f(T,\theta,d)$ describes the extent to which these step pairs differ. If $d=L/2$, then the two step pairs are statistically equivalent; any deviation is a signature of the alternating *SD* phase

We start the calculation of $\lambda_{\max}$ with a mean-field type of estimate, disregarding correlations of neighboring step pairs by assuming $p(l_i,l'_i)\approx p(l_i)p'(l'_i)$, where $p(l_i,l'_i)$ is the probability of simultaneously having terrace sizes l_i and l'_i. In a final step this result is improved by vector iteration with the full transfer matrix, allowing for additional anticorrelation of the terrace widths l_i and l'_i. However, the corresponding correction of the free energy away from the phase transition is quite small.

We can immediately get a qualitative picture of the nature of the phase transition here from Fig. 2, which shows the dependence of the free energy $f(T,\theta,d)$ on d, i.e., on

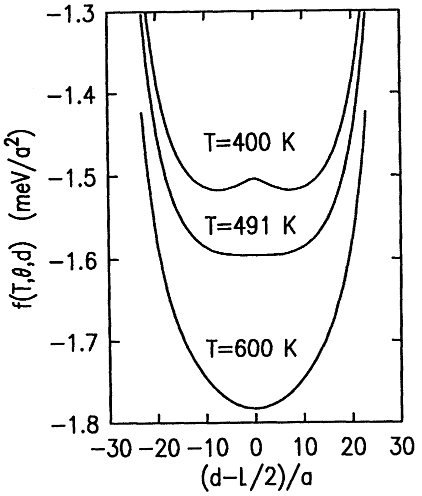

FIG. 2. Free energy per (1×1) surface unit cell for a given separation of the S_A steps, vs the deviation of this separation d from the symmetric (equidistant) value $d=L/2$. The miscut angle is $\theta=1.45°$ and the temperatures were chosen to be below, near, and above the critical point in the phase diagram.

the degree of step alternation, at different temperatures. At finite temperature, because of step meandering, the distinction between S and D steps is not unambiguous. However, at low temperature the minimum of f in Fig. 2 occurs for $d\neq L/2$, i.e., for adjacent step pairs alternating between S-like and D-like. The latter has also been verified by direct inspection of the probability distributions for the 2×1 terrace sizes of both step pairs.

As the temperature rises, the distinction between S and D becomes smaller, and so the (thermally averaged) elastic energy gained by SD alternation falls; meanwhile the SD configuration becomes less favorable for entropic reasons. At the highest temperature in Fig. 2, entropy clearly wins, and the lowest f occurs for the symmetric configuration.

To explain the procedure for constructing the complete phase diagram, the angle dependence of $f(T,\theta)$ is shown in Fig. 3. At low angles we observe a symmetric (i.e., $d=L/2$) phase of S steps, at high angles a symmetric phase of steps of predominantly D character, and in between the asymmetric SD phase. As we explicitly allow for periodicities only up to two step pairs, Gibbs's construction formally gives two coexistence regions: one of S and SD, and one of SD and D phases. However, from our earlier more detailed study of the $T=0$ case [17], we know that there really is no coexistence of phases. Instead, these coexistence regions have to be interpreted as (quite good) approximations to those parts of the phase diagram where the more complicated ordered phases (length ≥ 3 step pairs) of mixed S and D steps occur.

The resulting phase diagram is shown in Fig. 4. The open circles have been determined as described above, i.e., by Gibbs's construction at each temperature as depicted in Fig. 3. Note that the boundaries of the pure S, D, and SD phases agree well with the earlier $T=0$ ("devil's staircase") results [17], shown as squares. Some other points near T_c were derived in a different way. For example, the diamonds were obtained from temperature scans. However, at temperatures above $T_c\approx 490$ K the curves of free energy versus tan(θ) are convex, and d equals $L/2$ for all values of θ. Thus there is no phase transition above this critical temperature.

This picture of the phase transition implies a very different interpretation of experimental results. The freeze-in temperature of step structures on Si(001) is

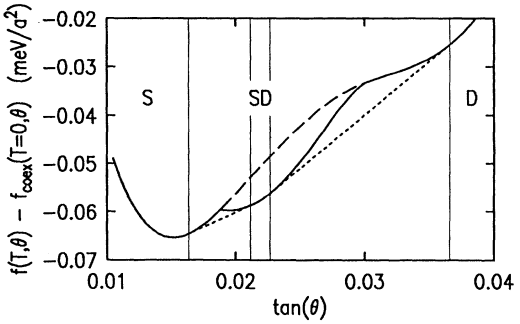

FIG. 3. Free energy per surface unit cell vs tanθ for $T\approx 0.9T_c$, and Gibbs's construction. For ease of viewing, a linear function of tanθ (arbitrarily chosen to equal the $T=0$ coexistence curve between pure S and D phases) has been subtracted from the data. Solid line: free energy $f(T,\theta)$. Dashed line: free energy $f(T,\theta,d=L/2)$ for equidistant S_A steps, i.e., suppressing SD alternation. Dotted line: (formal) Gibbs's construction for coexistence of S and SD or of SD and D phases. Existence regions for the pure phases are marked. See text for the correct physical interpretation of coexistence regions.

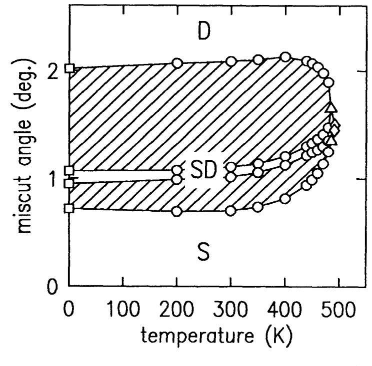

FIG. 4. Phase diagram for vicinal Si(001) surfaces. The thin center region corresponds to an SD phase, and the outside region to the symmetric phase, which at low temperature may be interpreted as S and D phases. In the intervening regions, more complicated mixed ordered phases are expected. The boundaries of the pure-phase regions agree well with results of an earlier more elaborate treatment at $T=0$, represented by squares.

generally believed to be around 800 K [9,21]. If the result that $T_c \approx 490$ K is even roughly correct (or is too high), then the experiments measure surfaces equilibrated above the critical temperature, where there is, in fact, no phase transition. This would reconcile the theoretical predictions of a phase transition with the experimental observations of only continuous behavior.

Because of uncertainty in the values of the parameters which enter the elastic model, we cannot rule out the possibility that T_c could be above 800 K. However, the phase transition might still be extremely hard to observe experimentally. Even at $T=0$, the transition takes place through a quasicontinuous sequence of weak first-order transitions [17], so that properties such as surface energy or terrace asymmetry should vary in a nearly continuous manner. At higher temperatures, this will be all the more true. Thus in the presence of experimental noise, there might be no observable qualitative difference between the behavior above and below the critical temperature.

We are grateful to D. P. DiVincenzo for discussions, and to P. A. Bennett and W. Ranke for providing preprints of their work prior to publication. This work was supported in part by ONR Contract No. N00014-84-C-0396.

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