Finite-Temperature Phase Diagram of Vicinal Si(100) Surfaces

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The phase diagram of vicinal Si(100) as a function of misorientation angle and temperature is calculated. Contrary to previous suggestions that only double-layer steps should appear on the equilibrium surface, it is predicted that the single-layer stepped surface is at equilibrium for small misorientation angles. This structure is stabilized by strain relaxation and by the thermal roughening of the steps. For annealed surfaces the critical angle at which the transition between the single- and double-layer stepped surface occurs is calculated to be $\theta_c \approx 2°$.

A vicinal crystal surface, i.e., one that is slightly misoriented with respect to a low-index direction, typically consists of terraces of the low-index direction and steps that accommodate the misorientation. Vicinal surfaces can exhibit different structural phases, since steps of different types may be favored depending on temperature T or angle of misorientation θ. Besides their intrinsic interest, stepped surfaces play a central role in important problems in physics and chemistry, including epitaxy, crystal growth, surface chemistry, and catalysis. In this Letter we study the equilibrium structure of the vicinal Si(100) surface and calculate its phase diagram as a function of θ and T. This surface has received particular attention largely because it is used as a substrate in the epitaxial growth of GaAs and other III-V compounds,[1] and is a prototypical system to study step-flow mechanisms of crystal growth.

The central result in this Letter challenges a basic assumption that is commonly adopted about the structure of vicinal Si(100). Previous experimental[2-9] and theoretical work[10,11] has led to the belief that this surface has only one equilibrium structure, where only biatomic or double-layer (DL) steps are present. It is shown here, however, that for small values of θ the equilibrium surface is characterized by monatomic or single-layer (SL) steps. These two phases of the surface are separated by a line of first-order transitions. This result has important consequences for the growth of GaAs on Si(100), since DL steps are thought to promote the growth of high-quality GaAs while SL steps may lead to antiphase domains.[1] The equilibrium phase diagram of the surface that is calculated here is consistent with new experimental data that are otherwise unexplained, and brings together into a coherent picture all the existing data known to us on the domain structure of vicinal Si(100).

The Si(100) surface reconstructs by forming surface dimers that are arranged in parallel rows.[12,13] The dimers can be oriented along two possible directions, depending on the plane where the crystal is cut. Thus the

surface has two degenerate reconstructed phases; they are related by a 90° rotation and their surface periodicity is either 2×1 or 1×2. Consider now a Si(100) surface that is slightly misoriented towards the [011] azimuth by an angle θ (the resulting steps are then oriented either parallel or perpendicular to the surface dimers). The surface misorientation can be accommodated by SL or DL steps,[14] leading to surfaces that are not only different in the height of the steps and the width of the terraces, but also in their basic lattice structure (see Fig. 1). The SL stepped surface has a two-sublattice structure with terraces of both 2×1 and 1×2 periodicity, while on the DL stepped surface all the terraces have the same orientation and is a so-called primitive surface. Experimentally it is observed that for $\theta \gtrsim 4°$ a surface that originally exhibits domains of 2×1 and 1×2 periodicity becomes primitive after careful annealing.[2-9] SL steps disappear in favor of DL steps. It is this property that makes stepped Si(100) preferable over flat surfaces for epitaxial
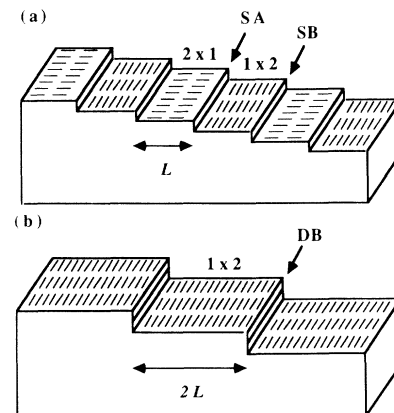

FIG. 1. Schematic representation of the (a) single-layer and (b) double-layer step structures of a vicinal Si(100) surface. The surface misorientation θ is related to the terrace width L by $\tan(\theta) = z_{SL}/L$, where $z_{SL} = 1.36$ Å is the height of a single-layer step.

growth, since primitive surfaces are difficult to obtain on nominally flat Si(100). In an effort to explain the observed preference of DL steps over SL steps, Aspnes and Ihm,[10] and later Chadi,[11] calculated the energies of different types of steps on Si(100). Both studies found DL steps to be energetically favorable over SL steps on a vicinal surface.

Compared with these previous studies, there are two new elements that are incorporated in this work. The first is a strain relaxation that occurs when the terraces alternate orientation and their surface stress tensor is anisotropic. The second is the effect of thermal fluctuations or roughening of the surface steps.

First let us consider the energy difference E between the SL and the DL stepped Si(100) surfaces at $T=0$. Finite-temperature effects will be added later. There are two contributions to E:

(1) Step energies.—There are two types of SL steps and also two types of DL steps on Si(100). On a vicinal SL stepped surface, terraces of 2×1 and 1×2 orientation as well as both types of SL steps alternate down the surface [see Fig. 1(a)]. A step of type SA connects a higher 2×1 terrace with a lower 1×2 terrace, and a step of type SB connects a higher 1×2 terrace with a lower 2×1 terrace. The bonding topology of these steps is different. For SA steps, the dimers on the upper terrace are perpendicular to the step edge, and for SB steps they are parallel. Calculations[11,15] show that $\lambda_{SB}\gg\lambda_{SA}$, where λ_{SA} and λ_{SB} are the energies (per unit length) of SA and SB steps, respectively. On a DL stepped surface all the terraces have the same orientation, and only one type of DL step is required [see Fig. 1(b)]. Experimentally[2-9] only the DL step where the surface dimers are parallel to the step edge are observed, corresponding to a 1×2 primitive surface. This step will be denoted by DB, and its energy by λ_{DB}. Calculations show that the second type of DL step, denoted by DA, has much higher energy.[11,15]

(2) Strain relaxation energy.— From elasticity theory it can be shown that a crystal surface with degenerate phases and anisotropic surface stress tensor can lower its energy with respect to a uniform one-domain surface by forming an ordered domain configuration.[16] The reduction in energy comes from a long-range elastic or strain relaxation in the semi-infinite medium that is driven by the difference in surface stress of the domains.[16,17] Microscopic calculations show that the surface stress tensor of Si(100) is anisotropic:[16,18] The surface is under tensile stress σ_1 parallel to the surface dimers and under compressive stress σ_2 in the perpendicular surface direction. The surface-stress anisotropy is calculated to be $\sigma_1-\sigma_2=1.0$ eV/a^2, where $a=3.84$ Å is the surface lattice constant. Thus the formation of 2×1 and 1×2 domains on Si(100) is energetically favored. The resulting equilibrium equations[16] were used to explain the surprising observations of Men, Packard, and Webb[19] of the behavior of this surface under applied external strain. These results also extend to the vicinal Si(100) surface.

The DL stepped surface is a one-domain structure where all the terraces have the same orientation, and no strain relaxation occurs. On the other hand, a SL stepped surface has terraces whose orientation alternates, rotating the stress tensor of the surface by 90° at each SL step. This leads to a strain relaxation energy (per unit area) for the SL stepped structure that has the form[16]

$$E_{\text{strain}}(L)=L^{-1}\lambda_\sigma\ln(L/\pi a),\qquad(1)$$

where L is the width of the terraces.[20] The parameter λ_σ (energy per unit length) is determined by the surface-stress anisotropy $(\sigma_1-\sigma_2)$, the elastic constants of the medium (silicon), and the geometry of the domains.

The energy difference between the SL and the DL stepped configurations of a vicinal Si(100) surface with misorientation θ is thus

$$E(L)=L^{-1}[(\lambda_{SA}+\lambda_{SB}-\lambda_{DB})/2-\lambda_\sigma\ln(L/\pi a)].\quad(2)$$

L and θ are related by $\tan(\theta)=z_{\text{SL}}/L$, where $z_{\text{SL}}=1.36$ Å is the height of a SL step. In principle, the interaction energy of direct step-step repulsion should also be included in Eq. (2). However, this energy scales[21] as $1/L^3$, and therefore the energetics of the surface is dominated by the logarithmic E_{strain} for small values of θ, which is the limit of interest here. Thus the $1/L^3$ step-step interaction energy will be neglected.

The step-energy difference in Eq. (2) is calculated to be[11,15] $\lambda_{SA}+\lambda_{SB}-\lambda_{DB}=110$ meV/a, favoring the DL stepped surface. For sufficiently large values of L, however, E_{strain} stabilizes the SL stepped surface. The condition $E(L)=0$ defines a first-order phase transition at

$$L_c=\pi a e^{(\lambda_{SA}+\lambda_{SB}-\lambda_{DB})/2\lambda_\sigma}.\qquad(3)$$

At this point the energy gained by strain relaxation is equal to the energy cost of introducing SL steps instead of the lower-energy DL steps. The SL stepped surface has lower energy for $L>L_c$ (or $\theta<\theta_c$), and the DL stepped surface has lower energy for $L<L_c$ (or $\theta>\theta_c$). For a geometry of striped domains as in Fig. 1 and $\sigma_1-\sigma_2=1.0$ eV/a^2, the parameter in E_{strain} is $\lambda_\sigma=11.5$ meV/a.[16] Using this number in Eq. (3) yields $L_c\approx1500$ Å, or equivalently $\theta_c\approx0.05°$. Such a small value of θ_c implies that the SL steps would most probably never be observed on an *equilibrium* stepped surface. This result, however, is for $T=0$.

At $T>0$ fluctuations must be taken into account. For the temperatures of interest here $(T\ll T_{\text{melting}})$ the most relevant thermal fluctuations are the formation of kinks along the steps and their associated roughening. At $T=0$ the steps occur as straight lines, but at finite temperatures they meander about the $T=0$ direction. To obtain a detailed description of the step roughening a series of scanning tunneling microscope (STM) images of the Si(100) surface were generated. A typical image of a SL stepped surface is shown in Fig. 2. This image of the surface is similar to ones obtained by others[8,13,22-24] at different length scales and provides important insight into the characteristic fluctuations of each

type of surface step. In particular, note that the *high-energy* SB steps undergo large fluctuations, while the *low-energy* SA steps remain relatively straight.

A simple model Hamiltonian will be used to study the statistical mechanics of the surface steps. The energy associated with the fluctuations of a step is taken to be given by

$$H = \sum_i (\lambda_\perp \mid h_i - h_{i-1} \mid + \kappa h_i^2) , \tag{4}$$

where h_i is the position of the step with respect to its $T = 0$ line at the point i along this line (in units of a dimer length). h_i represents the fluctuations in the profile of a step in units of surface dimers, and can take positive or negative integer values. The first term in H is the energy cost associated with the increase in the length of the step in the direction perpendicular to the $T = 0$ line. $\lambda_\perp$ is the energy per unit length of a step segment in this direction. The quadratic energy term in H has its origin in the strain relaxation energy E_{strain} of Eq. (1). It only applies to SL steps, since $E_{strain} = 0$ for the DL stepped surface. E_{strain} has its minimum for a surface with equally spaced steps. In the presence of fluctuations this perfect periodicity is broken, with an associated cost in strain energy. This leads to the quadratic term in h_i, which is derived from the equilibrium equations of the surface.[16] The spring constant κ of Eq. (4) is related to the stress parameter λ_σ of Eq. (2):[16] $\kappa = \lambda_\sigma (\pi a)^2 / 8L^2 = 14.2(a/L)^2$ meV/a. Note that $\kappa \sim 1/L^2$, and thus fluctuations are more strongly inhibited as the width of the terraces decreases.

This model for the fluctuations of the steps, together with their energies, can explain their observed roughening behavior. For SA steps the perpendicular segments of steps in a fluctuation are of the SB type: $\lambda_\perp(SA) = \lambda_{SB}$. Step-energy calculations show that $\lambda_{SA} = 10$

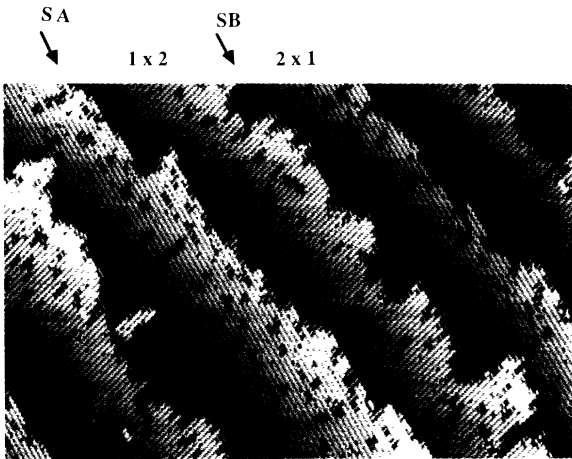FIG. 2. STM image of a single-layer stepped Si(100) surface tilted towards [011] by $\sim 0.4°$. The terraces alternate in orientation and are separated by alternating SA and SB steps. A small misorientation towards [01$\bar{1}$] is also present, and thus the steps are not perfectly aligned with respect to the surface dimers.

meV/a and $\lambda_{SB}/\lambda_{SA} \approx 15$; thus the excitations of SA steps have high energy. The reverse is true, however, for SB steps, since $\lambda_\perp(SB) = \lambda_{SA}$, and therefore these steps have low-energy excitations. A similar argument applies for DL steps, since $\lambda_\perp(DB) = \lambda_{DA}$ and according to calculations $\lambda_{DB} = 50$ meV/a and $\lambda_{DA}/\lambda_{DB} \approx 11$. Therefore the excitations of DB steps also have high energy.

Thus the only relevant thermal fluctuations are the formation of kinks on SB steps. The other types of surface steps have only high-energy excitations. The dominant $T > 0$ effect on Eq. (2) is then the renormalization of λ_{SB} due to thermal roughening, and the difference in step free energies [replacing the first term in Eq. (2)] may change substantially with increasing T.

The calculation of the relative free energy $F(L,T)$ between the SL and the DL stepped configurations is now reduced to the calculation of the free energy of the SB steps, whose excitations are described by H. Since steps on Si(100) are observed not to cross, they can be treated independently. This property of the steps is contained in the model, since the κh_i^2 term in H forces the meandering step to be centered between its neighboring steps. Moreover, since $\kappa \sim 1/L^2$, this effective step repulsion becomes stronger as the terrace width decreases. Thus H describes a one-dimensional system with short-range interactions. Its partition function Z_H can then be calculated using the transfer-matrix method, where

$$\langle h \mid e^{\kappa h^2/2k_B T} e^{\lambda_\perp \mid h - h' \mid /k_B T} e^{\kappa h'^2/2k_B T} \mid h' \rangle \tag{5}$$

is the transfer matrix associated with H. The free-energy difference $F(L,T)$ can then be readily obtained. $F(L,T)$ has the same form as $E(L)$, except that λ_{SB} is replaced as

$$\lambda_{SB} \rightarrow \lambda_{SB} - (k_B T)^{-1} \ln Z_H . \tag{6}$$

The condition for the phase transition is $F(L_c,T) = 0$, which has the same form as Eq. (3) with the substitution of Eq. (6).

The results of these calculations are shown in Fig. 3. This is the phase diagram of vicinal Si(100) in the θ-T plane. The first-order phase-transition line $\theta_c(T)$ is determined by the equation $F(L_c,T) = 0$. The equilibrium phases above and below the $\theta_c(T)$ line are the DL and the SL stepped configurations, respectively. To test this prediction a series of STM scans of the Si(100) surface were analyzed by correlating the presence of SL and DL steps with the misorientation angle. The results of this analysis are summarized in Fig. 3, where a typical STM image of a DL stepped configuration is shown in the inset. The data in Fig. 3 also include other available experimental results where the surface has been annealed at high temperatures for long times, to assure that kinetic constraints have been eliminated. The measured structure at room temperature, however, is not at equilibrium. Rather, it reflects the equilibrium structure at some higher, freezing-in temperature. From different experiments on epitaxial growth[25,26] this freezing-in temperature is estimated to lie between 450 and 550 K (note
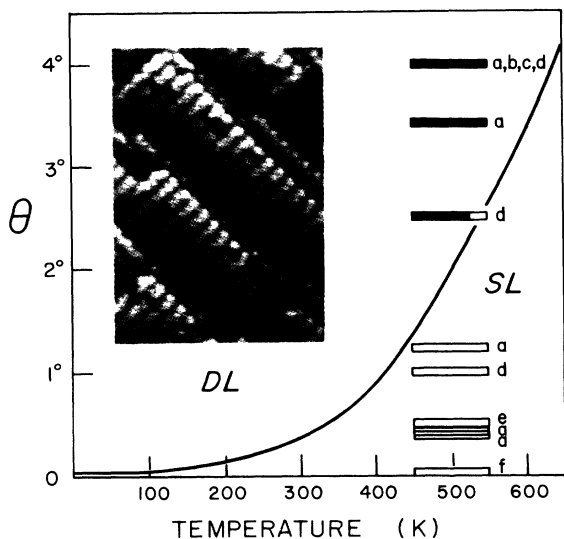
FIG. 3. Phase diagram of vicinal Si(100). The solid curve is the theoretically predicted line of first-order transitions between the single-layer (SL) and double-layer (DL) stepped configurations. At $T=0$, $\theta_c =0.05°$. Open and solid bars represent experimental observations of SL and DL stepped surfaces, respectively. The bar at $\sim 2.5°$ represents observation of a mixed phase with mostly DL steps. The horizontal range of the data is an estimate of the temperature where fluctuations of the steps are frozen. Inset: STM image of DL stepped Si(100) surface with $\theta \approx 3.5°$. [(a) this work, (b) Ref. 8, (c) Ref. 9, (d) Ref. 24, (e) Ref. 23, (f) Ref. 28].

that only mass transport *along* the steps is required in the fluctuations of the steps, but not mass transport across the terraces). The agreement between theory and experiment is satisfactory. The theory predicts that for annealed surfaces the transition between the SL and DL stepped surfaces is in the range $\theta_c \approx 1.2°$-$2.5°$. The experimental data place upper and lower bounds of $1°$ $\lesssim \theta_c \lesssim 3.5°$. Moreover, the experiment that reports a mixed phase at $\theta \sim 2.5°$ (Ref. 24) may be evidence, via a coexistence region, of a first-order transition. The data point at $\theta \approx 0°$, which originally was reported as a primitive surface,[27] has most recently been found to be unstable to the formation of 2×1 and 1×2 domains.[28]

It should be noted that if λ_{SA} were larger than the calculated value of 10 meV/a, as some experiments might suggest,[24] then the transition line $\theta_c(T)$ in Fig. 3 would be flatter. Also, on a surface with many missing dimers the surface stress might be screened, leading to a weaker stress coupling λ_σ and lowering the value of $\theta_c(T)$.

Finally, Monte Carlo simulations of the step Hamiltonian H yield step profiles similar to the experimental results shown in Fig. 2. These and other results will be presented in a longer publication.

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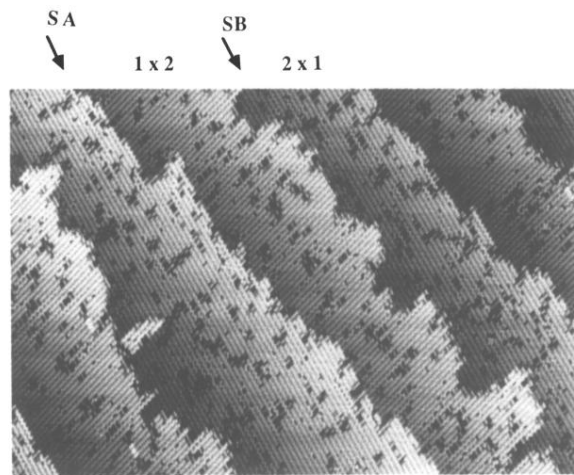
SA   SB
1 x 2   2 x 1

FIG. 2. STM image of a single-layer stepped Si(100) sur-
face tilted towards [011] by ~0.4°. The terraces alternate in
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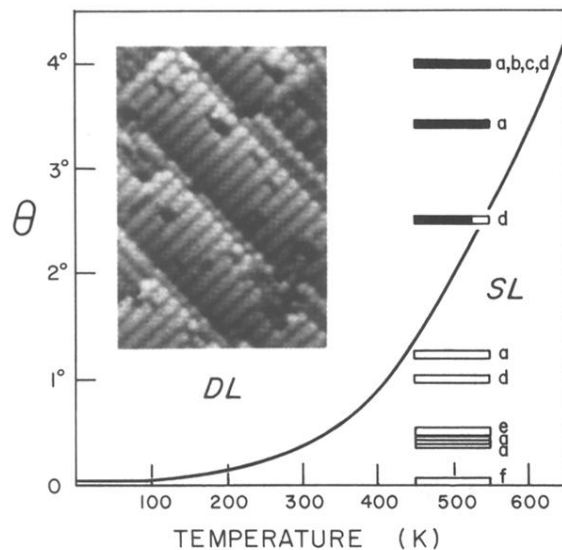dimers.

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