

Chapter 3. Semiconductor Surface Studies

Academic and Research Staff

Professor John D. Joannopoulos, Dr. Efthimios Kaxiras, Dr. Oscar L. Alerhand, Dr. Robert D. Meade

Graduate Students

Tomas A. Arias, Kyeongjae Cho, Mark F. Needels, Andrew M. Rappe, Jing Wang

3.1 Introduction

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Understanding the properties of surfaces of solids and the interactions of atoms and molecules with surfaces has been of extreme importance both from technological and academic points of view. The recent advent of ultrahigh vacuum technology has made microscopic studies of well-characterized surface systems possible. The way atoms move to reduce the energy of the surface, the number of layers of atoms involved in this reduction, the electronic and vibrational states that result from this movement, and the final symmetry of the surface layer are all of utmost importance in arriving at a fundamental and microscopic understanding of the nature of clean surfaces, chemisorption processes, and the initial stages of interface formation.

The theoretical problems associated with these systems are quite complex. However, we are currently at the forefront of being able to solve for the properties of real surface systems (rather than simple mathematical models). In particular, we are continuing our goal of calculating the total ground-state energy of a surface system from "first principles," so that we can provide accurate theoretical predictions of surface geometries. Our efforts in this program have concentrated in the areas of surface growth, surface reconstruction geometries, structural phase transitions, and chemisorption.

3.2 Microscopic Model of Heteroepitaxy

Epitaxial growth of dissimilar semiconductor materials holds significant potential for technological applications and has been the subject of major international efforts in recent years. Nevertheless, relatively little theoretical work has been performed to understand the fundamental interactions governing the initial stages of growth and the struc-

ture of the first few monolayers in these systems. Of particular interest is the prototypical system involving growth of GaAs on Si(100) substrates. Experimental studies have shown that on slightly miscut (vicinal) Si surfaces GaAs initially grows in an islandlike or three-dimensional mode in the vicinity of *stationary steps*. This is in contrast to both the usual planar or two-dimensional epitaxial mode which proceeds by step motion, as well as the conventional three-dimensional modes driven by strain or absence of wetting. In this work, we have developed a microscopic theoretical model which, for the first time, can explain the fundamental mechanism for this new type of three-dimensional heteroepitaxial growth. The model, supported by total-energy calculations, provides a stage-by-stage description of growth on surface steps, including the driving chemical and rehybridization reactions. It clearly shows the crucial role of double-layer steps (DLS) on the Si surface in initiating the growth of three-dimensional GaAs islands and inhibiting layered epitaxial growth.

The essential physical and chemical concepts which underlie the construction of our model are based on the following observations. First, both Ga and As can form passivated structures with threefold or fourfold coordination. When Ga and As atoms are fourfold coordinated, it is important that they form nearest-neighbor pairs to satisfy charge neutrality requirements. Threefold coordinated Si on the other hand typically has an energetically unfavorable dangling bond. Second, last year we demonstrated that on flat regions of the Si(100) surface a mixed GaAs overlayer phase (formed by switching like-atom bonds to unlike-atom bonds) is energetically favored and inhibits further growth of bulk GaAs along the [100] direction. Thus, there is a strong tendency for mixing at the initial stages which needs to be overcome in any viable model of growth. Finally, idealized growth of GaAs along the [100] direction would lead to physically unacceptable large electric fields due to a net interface charge.

With these ideas in mind, we proceed now to introduce the model of growth. The discussion will follow a realistic sequence of the growth stages as As and Ga atoms are deposited on the Si

surface. We begin with the clean Si surface, which when cut slightly off axis from the (100) orientation, necessarily contains steps. Of the various possible step configurations, we focus on the DLS, which have the appealing feature that they naturally eliminate antiphase domains. Moreover, theoretically it is found that DLS are the lowest-energy steps, and indeed surfaces can be prepared with only these steps present. Theoretical investigations indicate that the lowest-energy configurations for a DLS is as shown in figure 1(a). On this step there is a row of threefold coordinated Si atoms (shown with darker shading) which do not participate in dimer formation. As such, they are more reactive and less stable energetically.

In the usual experimental setup for MBE growth, the ambient pressure of As leads to an As-covered Si surface even before atomic beams are supplied for growth. On the flat regions of the Si substrate the As atoms break the existing Si dimers and form new As dimers. The ensuing threefold coordination of the As atoms and fourfold coordination of the underlying Si atoms is electronically passive and energetically very stable. To obtain the optimal configuration, however, one has to allow for proper bonding of the row of threefold coordinated Si atoms at the steps. We propose that this can be achieved by interchanging these threefold-coordinated Si atoms with As atoms and incorporating the appropriate amounts of As to complete the coverage of the surface. This substitution leads to the novel configuration shown in figure 1(b).

The next step in the growth model consists of depositing Ga on the surface. In the flat regions of the surface, the Ga atoms will break the As-As bonds and form a very low-energy mixed bilayer, with roughly equal amounts of Ga and As atoms in each atomic layer. Thus, growth of zinc-blende GaAs on the flat regions of Si(100) is suppressed.

The new element in the present approach is the influence of the step topology which prevents mixing in the immediate neighborhood of the steps and eventually promotes three-dimensional growth. To see this, first consider the row of Si atoms at the step in which each Si atom is surrounded by three As atoms as shown in figure 1(b). Electronegativity arguments indicate that it is energetically favorable to replace these Si atoms by Ga atoms. The removed Si atoms are allowed to diffuse to bulk positions of lower energy or to equivalent surface sites. The Ga-for-Si substitution creates pairs of fourfold-coordinated Ga and As atoms at the step edge, as shown in figure 1(c). Additional Ga atoms are incorporated between As-As bonds on either side of the step. Each Ga atom becomes threefold coordinated,

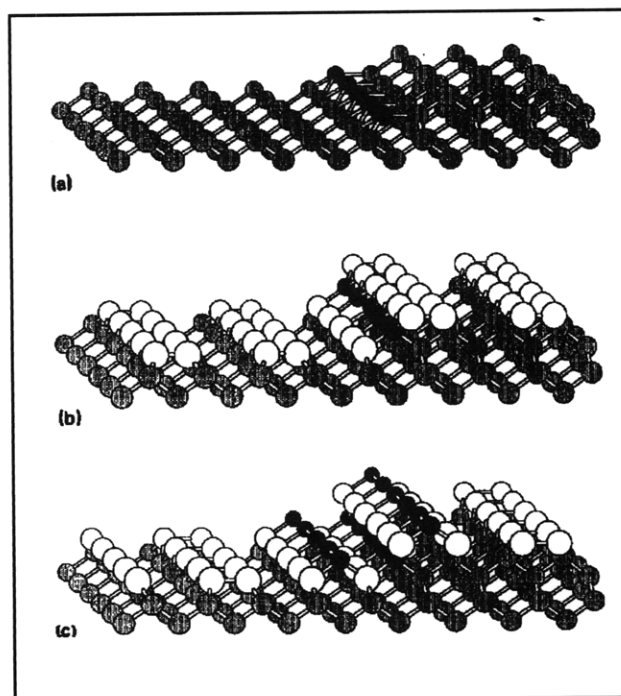


Figure 1. Three stages of growth of GaAs and DLS on Si(100): (a) The clean Si(100) surface with a DLS. The Si dimers on either side of the step are oriented parallel to the step. The threefold coordinated Si atoms at the step (shown by a darker shading) do not participate in dimer formation and should be more reactive. (b) The As-covered configuration. The row of threefold coordinated Si atoms at the step of the clean surface have been substituted by As atoms. The displaced Si atoms (shown by darker shading) are now fourfold coordinated and are bonded to three surface As atoms. (c) The Ga-and-As covered step configuration. Note that adding more Ga atoms on either side of the step would permit mixing which would inhibit (100) growth. Thus, preferred growth proceeds by growing larger and larger overlayers directly on the step along the (211) direction.

bonding to two As and one Ga. The As atoms on either side of the step remain threefold coordinated. Thus, the new structure is again electronically passive. But now, mixing is not energetically favorable to occur in this or any other subsequent overlayer configuration. This is because mixing at the step configuration cannot create more GaAs bonds in place of GaGa or AsAs bonds, which is the driving mechanism for mixing at the terraces. Avoidance of mixing is crucial if the growth of bulklike GaAs is to continue. The structural feature which leads to elimination of mixing is the creation of the Ga-As fourfold-coordinated pairs at the edge of the step. This feature, as a direct consequence of the geometry of the As-covered configuration, is not only intrinsically very stable, but crucial in promoting growth on the step. We emphasize that this is very different from the typical epitaxial growth process where adsorbed

atoms are continuously incorporated at highly reactive propagating steps.

We believe that these results are only the "tip of the iceberg," and we are currently pursuing further studies in this area.

3.3 Finite Temperature Phase Diagram of Vicinal Si(100)

The work described in this section was performed in collaboration with Professor A.N. Berker.

As discussed in the previous section, a vicinal crystal surface is one that is slightly misoriented with respect to a low-index direction and 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 work, 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 and is a prototypical system to study step-flow mechanisms of crystal growth.

The central result of this work challenges a common assumption about the structure of vicinal Si(100). Previous experimental and theoretical work has led to the belief that this surface has only one equilibrium structure, where only biatomic or double-layer (DL) steps are present. We find, 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. 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. 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, 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 figure 2). 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.

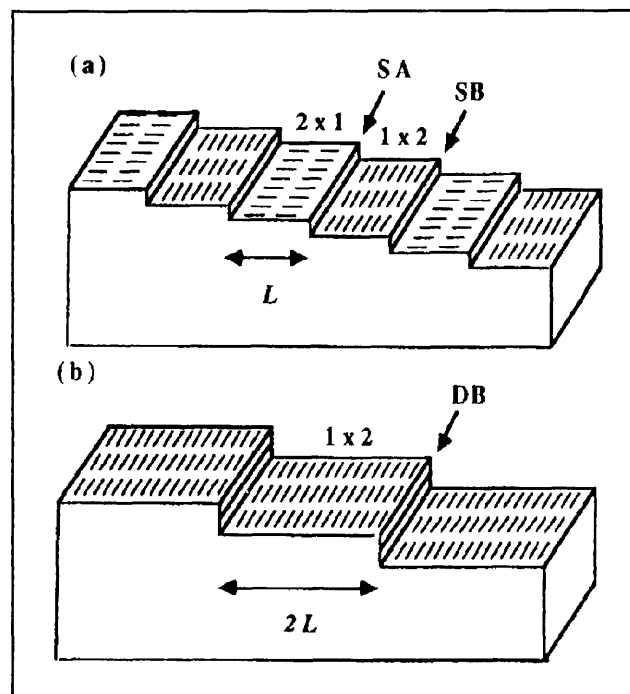


Figure 2. Schematic representation of the (a) single-layer and (b) double-layer step structures of a vicinal Si(100) surface. The surface misorientation θ is related to the terrace width L by $\tan(\theta) = z_{SL}/L$, where $z_{SL} = 1.36\text{\AA}$ is the height of a single-layer step.

Compared with these previous studies, there are two new elements that are incorporated into 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 figure 2(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. Our calculations 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 figure 2(b)). Our calculations show that $\lambda_{DB} \ll \lambda_{DA}$.
2. *Strain relaxation energy.* From elasticity theory we have proved 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. 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. Our calculations show that the surface stress tensor of Si(100) is anisotropic: The surface is under tensile stress σ_1 , parallel to the surface dimers and under compressive stress σ_2 in the perpendicular surface direction. Thus the formation of 2×1 and 1×2 domains on Si(100) is energetically favored.

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

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

The step-energy difference in eq. (1) is calculated to be $\lambda_{SA} + \lambda_{SB} - \lambda_{DB} = 110$ 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

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

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 geom-

etry of striped domains as in figure 2 and $\sigma_1 - \sigma_2 = 1.0$ eV/a², the parameter in E_{strain} is $\lambda_{\sigma} = 11.5$ meV/a. Using this number in eq. (2) yields $L_c \approx 1500$ Å, or equivalently $\theta_c \approx 0.05^\circ$. 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, holds only 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 figure 3. We note that the *high-energy* SB steps undergo large fluctuations, while the *low-energy* SA steps remain relatively straight.

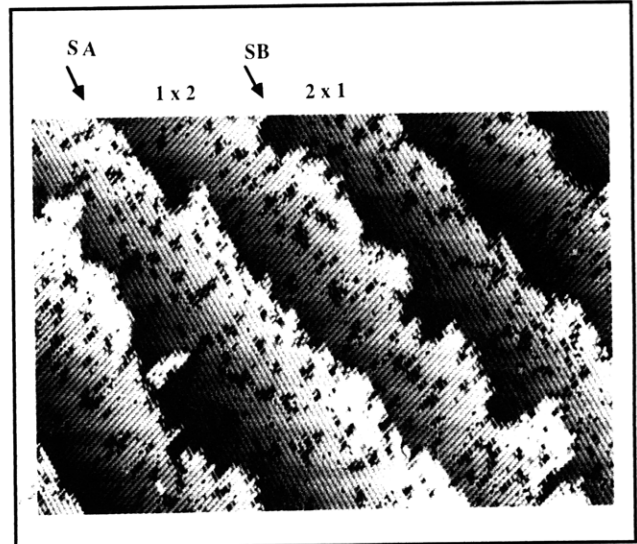


Figure 3. STM image of a single-layer stepped Si(100) surface tilted towards [011] by $\sim 0.4^\circ$. The terraces alternate in orientation and are separated by alternating SA and SB steps. A small misorientation towards [011] is also present, and thus the steps are not perfectly aligned with respect to the surface dimers.

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

$$H = \sum_i (\lambda_{\perp} |h_i - h_{i-1}| + \kappa h_i^2), \quad (3)$$

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. λ 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). 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. The spring constant κ of eq. (3) is related to the stress parameter $\kappa = \lambda_\sigma(\pi a)^2/8L^2 = 14.2(a/L)^2 \text{ meV}/a$. Note that $\kappa \sim 1/L^2$, and thus fluctuations are more strongly inhibited as the width of the terraces decreases.

The partition function Z_H associated with eq. (3) can now be calculated using the transfer-matrix method, where

$$\langle h | e^{kh^2/2k_B T} e^{\lambda|h-h'} | + k_B T e^{kh'^2/2k_B T} | h' \rangle \quad (4)$$

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

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

The condition for the phase transition is $F(L_c, T) = 0$. (5)

The results of these calculations are shown in figure 4. This is the phase diagram of vicinal Si(100) in the $\theta - T$ 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 figure 4, where a typical STM image of a DL stepped configuration is shown in the inset.

The data in figure 4 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, this freezing-in tem-

perature is estimated to lie between 450 and 550 K (note 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 the theory and experiment is satisfactory. The theory predicts that for annealed surfaces the transition between the S1 and DL stepped surfaces is in the range $\theta_c \approx 1.2^\circ - 2.5^\circ$. The experimental data place upper and lower bounds of $1^\circ \lesssim \theta_c \lesssim 3.5^\circ$. Moreover, the experiment that reports a mixed phase at $\theta \sim 2.5^\circ$ may be evidence, via a coexistence region, of a first-order transition. The data point at $\theta \approx 0^\circ$, which originally was reported as a primitive surface, has most recently been found to be unstable to the formation of 2×1 and 1×2 domains.

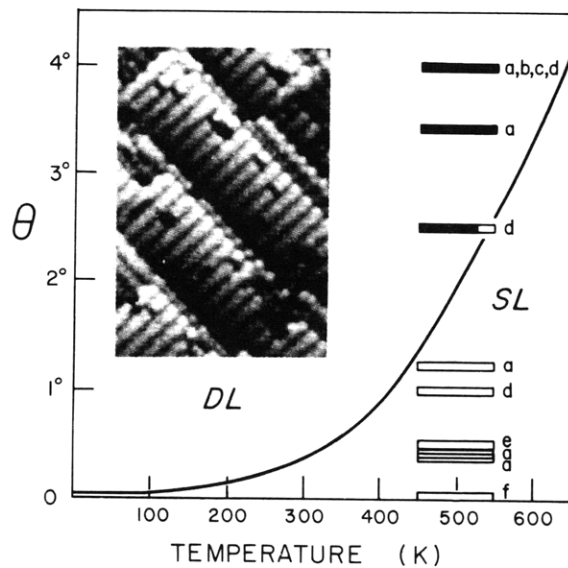


Figure 4. Phase diagram of vicinal Si(100). The solid curve is the theoretically predicted line of first-order transitions between the single-layer (SL) and double-layer (DB) stepped configurations. At $T = 0$, $\theta_c = 0.05^\circ$. Open and solid bars represent experimental observations of SL and DL stepped surfaces, respectively. The bar at $\sim 2.5^\circ$ represents observations 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 $\theta \approx 3.5^\circ$.

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