

Chapter 4. Semiconductor Surface Studies

Academic and Research Staff

Professor John D. Joannopoulos, Dr. Arnaldo Dal Pino, Dr. Robert D. Meade

Graduate Students

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

4.1 Introduction

Sponsor

Joint Services Electronics Program
Contract DAAL03-89-C-0001
Contract DAAL03-92-C-0001

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 solving for the properties of real surface systems. In particular, we are continuing toward 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.

4.2 Heteroepitaxial Growth

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. Since growth typically begins with an As overlayer, one first needs to understand this seemingly simple system. Experimentally, it is observed that the adsorption of As on a stepped Si(100) surface can drastically rearrange the distribution of steps of the original surface. These changes in surface morphology are controlled by different factors, including temperature, coverage of As, and the type and density of steps on the original surface. The structure of the the As-covered Si(100) surface [henceforth Si(100):As] determines many of the properties of the final epitaxial film.

In particular, it has been observed that GaAs grown epitaxially on Si(100) can have two orientations, related by a 90 degree rotation, with respect to the Si(100). This puzzling observation, the so-called sublattice-orientation (or allocation) dilemma, has not been understood. Naively, this could be explained if the first epilayer above the Si substrate could be selected to be a Ga or As layer. However, bond strength and other theoretical arguments, as well as experimental evidence, show this selective wetting of the Si(100) surface by As or Ga does not occur.

In this work we have performed theoretical calculations which show that As adsorbed on a vicinal Si(100) surface with double-layer steps either *can grow directly on top of the Si surface, or can rearrange the surface so that it replaces the original top Si layer*. The former structure is metastable and results from growth at low temperatures. The latter has lower energy and occurs for growth at substrate temperatures where surface diffusion is activated. Replacing adsorption by substitution changes the sublattice of the diamond structure exposed at the surface and corresponds to a 90 degree rotation of the crystal orientation about the surface normal. The resulting two configurations of the stepped Si(100):As surface are related by a 90 degree rotation, but otherwise differ only in the type of steps present at the surface. Their difference in energy, which we calculate from first principles, is related to the relaxation of stress at surface steps. This result shows that the rear-

rearrangement of steps upon As adsorption controls the orientation of an epitaxial GaAs film.

Both Si(100) and Si(100):As surfaces have 2×1 reconstructions where surface atoms (Si in the first case and As in the second) form dimers arranged in parallel rows. A simple picture for the adsorption of As on Si(100) is that the Si dimers break and As dimers are formed on top, perpendicular to the original Si dimers. This rotates the orientation of the surface dimers by 90° . A single-domain Si(100) 2×1 surface would result in a single-domain Si(100):As 1×2 surface. STM images show that the orientation of the As dimers depends on the substrate temperature T_s during deposition. For low initial temperatures ($T_s \leq 400^\circ\text{C}$) the surface reconstruction rotates from 2×1 to 1×2 , as the simple picture describes.

We begin by considering a single-domain Si(100) 2×1 surface, as typically used in growth experiments. These are obtained by using double-layer-stepped vicinal surfaces misoriented towards the [011] direction. Here we will restrict ourselves to the case where both the starting Si(100) and the final Si(100):As surfaces are double-layer stepped and the As coverage is one complete monolayer. These are the conditions relevant to typical growth conditions. On the clean Si(100) surface the Si dimers are parallel to the step edges. Double-layer steps with dimers perpendicular to the edge have much higher energy and are not observed. In principle, there are two types of double-layer steps on the Si(100):As surface. Type A, where the As dimers are perpendicular to the step edge [Figure 1(a)], and type B, where the As dimers are parallel to the edges [Figure 1(b)]. The reconstruction of the surface is 1×2 with type-A steps, and 2×1 with type-B steps. Figure 1 shows steps with a simple edge termination, where Si atoms are fourfold coordinated and As atoms are threefold coordinated with a doubly occupied lone-pair orbital. This is the same bonding configuration that passivates the flat Si(100):As surface. Other step reconstruction we considered, which are discussed later in this chapter, were found to have higher energies.

To determine the relative stability of the 1×2 and 2×1 stepped Si(100):As surfaces, we compare the energies of surfaces with type-A and type-B steps, respectively. We calculate total energies from first principles within the framework of density-functional theory in the local-density approximation, using norm-conserving pseudo-potentials.

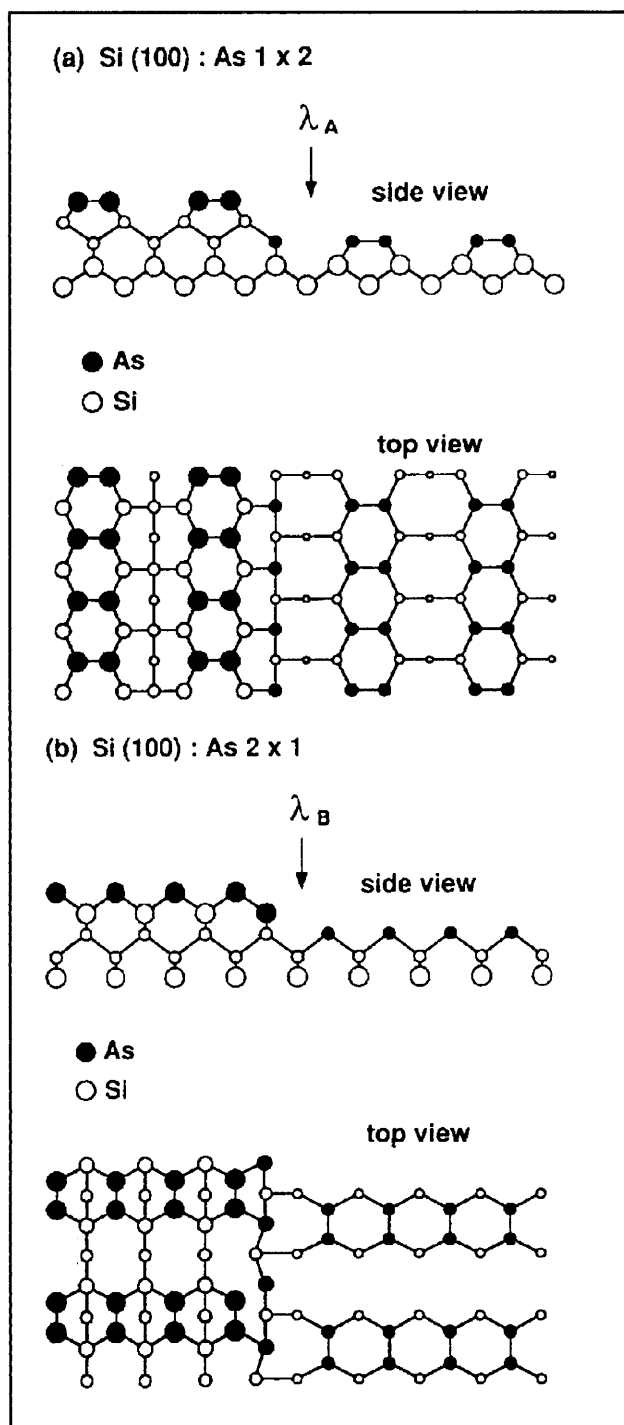


Figure 1. Top and side views of double-layer steps on Si(100):As surfaces. (a) Type-A steps: As dimers perpendicular to the step edge. (b) Type-B steps: As dimers parallel to the step edge (edge relaxation is illustrated in the top view, see text). Larger circles on top views represent atoms closer to the surface. The two circle sizes on side views represent front and back [011] planes.

The calculated energy difference between type-A and type-B steps of Si(100):As is

$$\lambda_A - \lambda_B = (200 \pm 20) \text{ meV/a}, \quad (1)$$

where λ_A and λ_B are the energies of type-A and type-B steps, respectively, and $a = 3.80\text{\AA}$ is the unit length along the step. This energy difference is large enough to change the surface from one step configuration to the other. Indeed, an energy difference of $\sim 110 \text{ meV/a}$ between single- and double-layer steps on vicinal Si(100) surfaces (for a surface misorientation larger than $\sim 3\text{-}4^\circ$) drives the surface to have a majority of double-layer steps. It should be noted that the calculated step energies represent step-formation plus step-step-interaction energies, and the large size of these systems makes it prohibitive to increase the separation between steps and systematically separate these two contributions. However, it is assumed that the latter is approximately eliminated from the problem by taking energy differences between stepped surfaces and that this difference does not change significantly with larger step separations.

An inspection of figure 1 shows no obvious electronic origin for the large energy difference between type-A and type-B steps. In both cases the Si and As atoms have ideal bonding configurations, and there is no particular atom or bond whose relaxation or rehybridization might explain this result. We find that the energy difference is related to the relaxation of surface stress. The Si(100):As surface is under a large tensile stress, both parallel and perpendicular to the As dimers, that results from the tendency of the As atoms to from 90 degree bond angles and pull themselves up from the surface. This stress introduces a torque on surface steps, which allows a lateral contraction of the surface in the region near the steps, at the expense of introducing bulk strain.

Figure 2 shows the response of type-A and type-B steps to the tensile surface stress. Type-A steps lead to a large lateral contraction. This contraction is $\sim 3.5\%$ for the first layer of Si atoms, most of it within two lattice constants from the step edge (see inset in figure 2), and decays to zero deeper into the bulk. The surface As dimers, perpendicular to the step edge, are $\sim 2\%$ shorter than their calculated value on a flat Si(100):As surface. The relaxation type-B steps is different, even though the strength the tensile stress is calculated to be approximately equal both parallel and perpendicular to the surface dimers [the large energy difference in equation (1) is consistent with this]. Figure 2 shows that type-B steps undergo almost no contraction. Still, the relaxed coordinates suggest that the surface stress has been significantly reduced. Although we have not directly calculated the stress remaining on the stepped

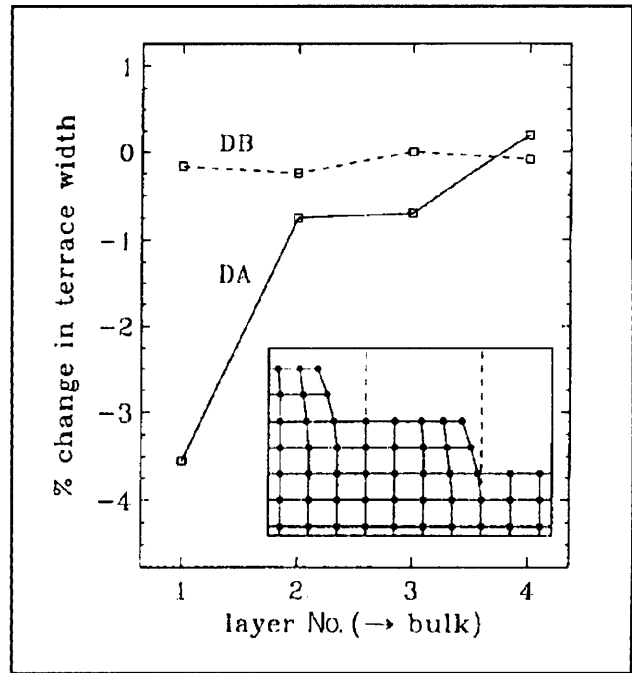


Figure 2. Layer-by-layer lateral contraction for a surface with type-A (solid line) and type-B (dashed line) steps as a function of penetrate into the bulk. Layer No. 1 denotes the first layer of Si atoms below the surface As dimers. Inset: Schematic representation of lateral contraction for a surface under tensile stress, defined with respect to the ideal terrace width shown by the vertical dashed lines.

surface (such calculations are beyond current capabilities), the lack of strain in the subsurface of type-B steps provides evidence of reduced surface stress. On flat Si(100):As subsurface strain forces a displacement of atoms from their ideal bulk positions. Atoms in third and fourth layers that are underneath surface dimers shift up, and subsurface atoms that are between dimer rows shift down. For type-A steps this distortion is further enhanced. On the other hand, for type-B steps the relaxed positions of the subsurface atoms are close to their ideal bulk value. This lack of strain in the subsurface for type-B steps is consistent with the reduction of surface stress.

We now address the implications of these results to growth experiments. Our calculations show that the Si(100):As 1×2 surface with type-A steps is a metastable structure. This surface results from the growth of As directly on top of the initial Si surface. Experimentally, it is obtained by depositing As at low substrate temperatures, where the As overlayer caps the surface and freezes any surface mobility. However, if the temperature is high enough during As deposition to activate surface diffusion, the surface can then reach the lower-energy configuration with type-B steps. This explains the surprising experimental observations. We note that this change in step type

requires a large rearrangement of the surface, but similar step redistributions requiring mass transport across the surface have been observed when the initial Si surface has single-layer steps. The transformation from type-A to type-B step may occur through other intermediate step configurations, including single-layer steps, and a complete conversion may not occur because of the large amount of mass transport required. This may further depend on the flux of As, and on whether As₂ or As₄ gas sources are used. Also, if surface diffusion is completely frozen or defects pin the edges of steps, type-A steps with a rebonded edge may occur on terraces that originally had an odd number of lattice sites, and both types of type-A steps may appear on the low-temperature surface. In principle, the surface with type-B steps ought to be reached from the surface with type-A steps upon annealing. However, As begins to leave the surface before this change occurs, and mixtures of steps with different heights are then observed.

It should be noted that since the driving force for the rotation of the As surface dimers is the difference in energy between type-A and type-B steps, as the surface misorientation becomes smaller and the density of steps decreases, the energy gain by step rearrangement diminishes. On nearly flat surfaces only the $2 \times 1 \rightarrow 1 \times 2$ change in orientation of Si to As surface dimers should be observed.

For the heteroepitaxial growth of GaAs on Si(100), our results predict the sequence of orientations of the Si and then As surface dimers in the growth process of Si(100)→Si(100):As→GaAs/Si(100). For low initial substrate temperatures, the predicted sequence is $2 \times 1 \rightarrow 1 \times 2 \rightarrow 4 \times 2$, and for high initial temperatures the sequence is $2 \times 1 \rightarrow 2 \times 1 \rightarrow 2 \times 4$. The final orientation of the GaAs epilayer depends on whether the equilibrium Si(100):As surface is attained, illustrating the interplay between kinetics and energetics in epitaxial crystal growth. This result explains the sublattice orientation dilemma and brings into a coherent picture experiments that seemed to be in contradiction. Also, type-A and type-B steps on Si(100):As may promote different nucleation channels for growth, leading to epitaxial films with different characteristics.

4.3 Molecules

In order to begin to address problems associated with molecules interacting with solid surfaces, it is important to test the applicability of the theoretical tools (developed for condensed matter systems) for isolated molecules. Moreover, if successful, these tools could be used to study large heterogeneous nonperiodic systems such as biological mol-

ecules that may consist of extended organic fragments, metal ions, and solvent water molecules. As a first step in this direction, *ab initio* theoretical calculations were performed on a large number of molecules with a variety of sizes and functional groups consisting of the first-row elements. These include the simple molecules H₂, H₂O, CH₄ and NH₃ that are constituents of the "biotic-soup" of the primordial atmosphere, neutral glycine which is the simplest amino acid, and formamide, which models the peptide-bond between amino acids in a protein.

Table I lists the results of our theoretical calculations (LDAP-PW) and compares them with both experimental values and quantum chemistry (MP2/6-31G*) Hartree Fock calculations.

Overall agreement of LDAP-PW with experiment and MP2 calculations is excellent. Average deviations from experiment and MP2 are 0.030Å and 0.034Å for bond lengths and 0.5 degrees and 1.0 degrees for bond angles. If the hydrogen-bonded system 3-hydroxy-acrylaldehyde is not included in the averages, the bond-length deviations become 0.017Å and 0.024Å respectively.

Upon closer examination, certain trends become apparent within the data contained in Table I. The most striking pattern is that a LDAP-PW calculation of a bond distance between two heavy (non-hydrogen) atoms is almost always closer to experiment than the corresponding MP2 result. Conversely, bonds involving at least one hydrogen are almost always calculated more accurately using MP2. In addition, bond angles which include zero or one hydrogen atom are almost always more accurate using LDAP-PW, while those including two hydrogens are usually better reproduced by MP2. We believe that these effects are due to the use of the LDA rather than a more accurate exchange-correlation functional. The small size of hydrogen makes its charge density change over a short length scale. It appears likely that gradient corrections to LDA will improve these results. Another trend which we have observed is that long bonds are reproduced more poorly than short bonds by the LDAP-PW. This effect is also probably due to the use of the LDA. As the atoms in a bond separate, they act more like free atoms, and the LDA does a poorer job on free atoms than on covalent materials. This effect is particularly striking in the O-O bond of H₂O₂ and the hydrogen bond in 3-hydroxyacrylaldehyde.

These results show that the LDAP-PW method can produce accurate structural parameters for molecules. The data suggest that the method which uses plane waves, pseudopotentials, and supercells may be a useful alternative to standard *ab initio* quantum mechanical methods for calcula-

Molecule	Parameter	Exp	MP2	Δ_e^1	LDAP-PW	Δ_e^2	Δ_G
H ₂	r(HH)	0.742	0.738	0.004	0.776	0.034	0.038
O ₂	r(OO)	1.208	1.242	0.034	1.183	0.025	0.059
N ₂	r(NN)	1.098	1.131	0.033	1.099	0.001	0.032
P ₂	r(PP)	1.893	1.936	0.043	1.875	0.018	0.061
CO	r(CO)	1.128	1.151	0.023	1.138	0.010	0.013
CO ₂	r(CO)	1.162	-	-	1.170	0.008	-
H ₂ O	r(OH)	0.958	0.969	0.011	0.976	0.018	0.007
	<(HOH)	104.5	104.0	0.5	104.0	0.5	0.0
CH ₄	r(CH)	1.092	1.090	0.002	1.102	0.010	0.012
NH ₃	r(NH)	1.012	1.017	0.005	1.028	0.016	0.011
	<(HNH)	106.7	106.3	0.4	105.7	1.0	0.6
PH ₃	r(PH)	1.420	1.415	0.005	1.440	0.020	0.025
	<(HPH)	93.3	94.6	1.3	91.6	1.7	3.0
H ₂ O ₂	r(OO)	1.452	1.467	0.015	1.414	0.038	0.053
	r(OH)	0.965	0.976	0.011	0.982	0.017	0.006
	<(OOH)	100.0	98.7	1.3	100.2	0.2	1.5
	ω (HOOH)	119.1	121.3	2.2	118.7	0.4	2.6
N ₂ H ₂	r(NN)	1.252	1.267	0.015	1.233	0.019	0.034
	r(NH)	1.028	1.036	0.008	1.052	0.024	0.016
	<(NNH)	106.9	105.4	1.5	107.2	0.3	1.8
H ₂ CO	r(CO)	1.208	1.221	0.013	1.205	0.003	0.016
	r(CH)	1.116	1.104	0.012	1.135	0.019	0.031
	<(HCH)	116.5	115.6	0.9	116.4	0.1	0.8
C ₂ H ₂	r(CC)	1.203	1.218	0.015	1.196	0.007	0.022
	r(CH)	1.061	1.066	0.005	1.058	0.003	0.008
HNC	r(NC)	1.169	1.187	0.018	1.178	0.009	0.009
	r(HN)	0.994	1.002	0.008	1.018	0.024	0.016
HNO	r(NO)	1.212	1.237	0.025	1.188	0.024	0.049
	r(HN)	1.063	1.058	0.005	1.093	0.030	0.035
	<(HNO)	108.6	107.3	1.3	109.2	0.6	1.9
Formamide (HCONH ₂)	r(CO)	1.193	1.224	0.031	1.217	0.024	0.007
	r(CN)	1.376	1.361	0.015	1.365	0.011	0.004
	<(OCN)	124.7	124.8	0.1	124.9	0.2	0.1
Glycine (NH ₂ CH ₂ CO ¹ O ² H)	r(C=O ¹)	-	1.218	-	1.204	-	0.014
	r(CO ²)	-	1.358	-	1.345	-	0.013
	r(CC)	-	1.515	-	1.535	-	0.020
	r(NC)	-	1.451	-	1.460	-	0.009
	<(O ¹ CO ²)	-	123.2	-	123.7	-	0.5
	<(O ² CC)	-	111.4	-	111.9	-	0.5
	<(O ¹ CC)	-	125.4	-	124.4	-	1.0
	<(CCN)	-	114.9	-	114.8	-	0.1
H ₂ PO ₄ ⁻¹	r(PO)	-	1.510	-	1.482	-	0.028
	r(P-OH)	-	1.680	-	1.640	-	0.040
	<(HO-P-OH)	-	101.1	-	101.2	-	0.1
	<(O-P-OH)	-	106.9	-	107.1	-	0.2
	<(O-P-O)	-	126.2	-	125.2	-	1.0
3-hydroxy- acrylaldehyde (HOCHCHCHO)	r(O-H)	0.969	0.994	0.025	1.079	0.110	0.085
	r(O...H)	1.680	1.694	0.014	1.418	0.262	0.276

Table I. A comparison of LDAP-PW geometry optimizations with experiment and with MP2. Δ_e^1 and Δ_e^2 are the deviations of the MP2 and LDAP-PW calculations from experiment, and Δ_G is the deviation of LDAP-PW from the MP2 values.

tions on chemical systems. Future work will include more realistic density functionals and tests of energetics of chemical transformations. In addition, research is continuing to develop more efficient energy minimization algorithms and superior pseudopotentials. These changes will improve the efficiency and accuracy of the method for the study of periodic and aperiodic chemical and biochemical systems.

4.4 Publications

- Alerhand, O., J. Wang, J.D. Joannopoulos, E. Kaxiras, and R. Becker. "Adsorption of As on Stepped Si(100): Resolution of the Sublattice Dilemma." *Phys. Rev. Rapid Comm.* B44: 6534 (1991).
- Alerhand, O., J. Wang, J.D. Joannopoulos, and E. Kaxiras. "Growth of As Overlayers on Vicinal Si(100)." *J. Vac. Sci. Tech.* B9: 2423 (1991).
- Arias, T., M. Payne, and J.D. Joannopoulos. "Precise and Efficient Ab-Initio Molecular Dynamics." *Phys. Rev. B.* Forthcoming.
- Joannopoulos, J.D., P. Bash and A. Rappe. "Modern Iterative Minimization Techniques in Quantum Chemistry." *Chem. Des. Automat. News* 6(8): pages (1991).
- Rappe, A., and J.D. Joannopoulos. "The Design of Convergent and Transferable Ab-Initio Pseudopotentials." *Proceedings of the Nato Advanced Study Institute*, Aussois, France, 1991.
- Rappe, A., J.D. Joannopoulos and P. Bash. "A Test of the Planewaves for the Study of Molecules from First Principles." *J. Amer. Chem. Soc.* Forthcoming.
- Wang, J., M. Needels, and J.D. Joannopoulos. "Surface and Fracture Energies in GaAs." In *Surface Physics and Related Topics*. Teaneck, New Jersey: World Scientific Publ., 1991. pp. 314.