# 10.0 Semiconductor Surface Studies

**Academic and Research Staff**

Prof. J.D. Joannopoulos, Dr. G. Gomez-Santos, Dr. E. Kaxiras, Dr. O. Alerhand

**Graduate Students**

T. Arias, M. Needles, A. Rappe, E. Tarnow, J. Wang

John D. Joannopoulos

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. Actually, one of the most difficult and fundamental problems in surface studies, both from the experimental and theoretical points of view is simply the determination of the precise positions of the atoms on a surface. Currently, there are many surface geometries, even for elemental surfaces, that remain extremely controversial.

The theoretical problems associated with these systems are quite complex. We are, however, currently in 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 may be able to provide accurate theoretical predictions of surface geometries. Our efforts in this program have concentrated in the areas of surface growth reaction pathways, surface reconstruction geometries, structural phase transitions, and hyrdogenation.

## 10.1 Surface Reconstruction Geometries

Using "first principles" total energy calculations, it is possible to determine on a microscopic scale how atoms behave when they are on the surface of a solid. This is a fundamental problem that has plagued both theorists and experimentalists for decades. The difficulty lies with the very strong interactions that may exist between the surface atoms and the host atoms constituting the rest of the solid. These interactions can strongly disturb the original idealized atomic arrangement at the surface changing the nature of the bonding and even the original stoichiometry.

In recent years there has been considerable activity focused on determining the exact equilibrium geometry of the [111] surfaces of the III-V compounds. In particular, the

($\overline{111}$) As-terminated surface of GaAs stands out as a system that is very poorly understood. Even the relative abundance of Ga and As atoms in the surface region is not established with sufficient accuracy. The multitude of diffraction patterns observed on this surface (e.g., (2x2), (3x3), ($\sqrt{19}$ x$\sqrt{19}$ )) and their sensitivity to preparation conditions make the problem very intriguing. The layer of exposed As atoms that constitutes the unreconstructed ($\overline{111}$) bulk plane is apparently unstable leading to a rich variety of surface reactions and atomic arrangements. No model has yet to emerge as a satisfactory candidate for any of these reconstructions.

In this work we have focused on the most stable observed pattern, namely the (2x2) reconstruction. The variety of structural models, for the reconstructions of this surface, that we have considered are shown in figure 10.1. The total energies for these structures, calculated as a function of the relative chemical potential of Ga and As atoms are summarized in figure 10.2.
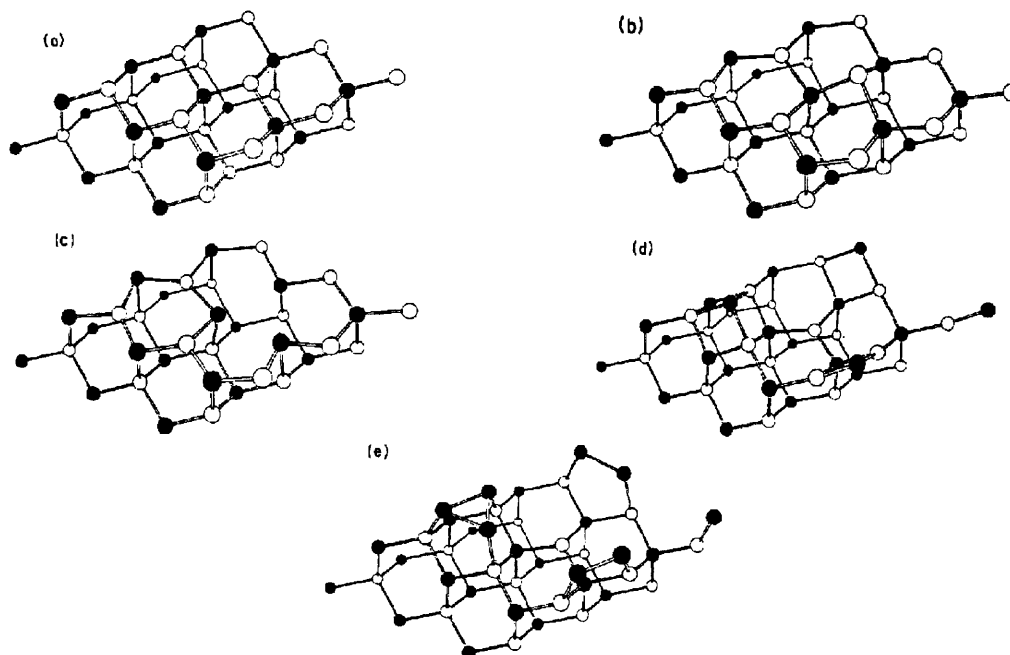


Figure 10.1. Structural models for the (111) surface (2x2) reconstructions. The first four atomic layers are shown in perspective. The atoms in each layer outline the (2x2) unit cell, in the ideal configuration. The same atoms and their nearest neighbors are shown in the other reconstructions. Solid circles represent As atoms and empty circles represent Ga atoms. (a) Ideal surface. (b) Buckled geometry; a variation of this is the substitutional geometry. (c) Vacancy geometry; variations of this are Ga-vacancy plus Ga-substitutional geometry and the Ga-vacancy plus As $p$ -bonded geometry. (d) Adatom geometry. (e) Triangle geometry.

From these results we can predict that phase transitions will occur, as the relative chemical potential scans its range, whenever two lowest energy lines cross and different reconstructions become the lowest energy configuration. Note that two such crossings occur in figure 10.2. The results presented here are for perfectly equilibrated surfaces and care must be taken to include kinetic effects which can be crucial in certain cases. Thus the very low sticking coefficient of As indicates it is unlikely that As-adatom models (either the single As adatom of the As-triangle) will be observable on the As-
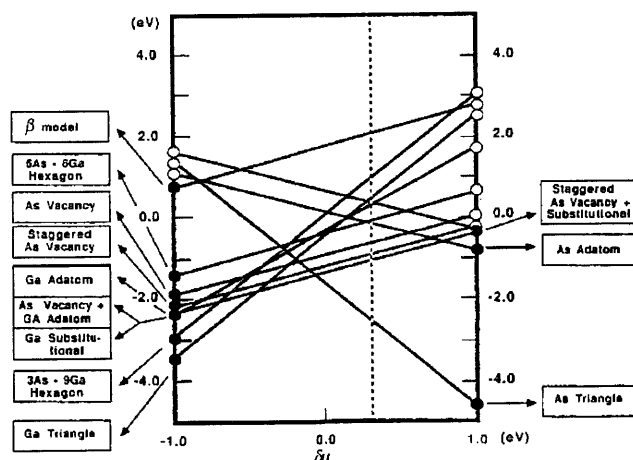
Figure 10.2. Energy versus relative chemical potential $\delta\mu$ of the different reconstruciton models of the $(\overline{1}\overline{1}\overline{1})$ surface. The range of $\delta\mu$ scans the values consistent with the Ga bulk and $As_2$ gas reservoirs. The closed dots are the calculated energies per (2x2) unit cell with respect to the ideal surface. The dashed line indicates the upper limit of $\delta\mu$ constistent with an $As_4$ gas reservoir.

terminated surface. It may, in fact, be rather difficult to simulate the surface As-rich environment at all. It is more reasonable to suggest that an experimentally observed As-rich reconstruction should be one of the two lowest energy geometries in the $-0.3 < \delta\mu < -0.1$ eV range. That is, either the staggered As vacancy or the Ga-adatom configurations. We are inclined to favor the staggered As vacancy. On the other hand, the Ga-rich reconstruction is most certainly the Ga-triangle, both from energetic and structural considerations. It is the lowest-energy geometry among all the negative stochiometry models and presents the most favorable coordination once all the surface As and part of the surface Ga has been removed.

# 10.2 Structural Phase Transitions

All the calculations described in the previous section were at zero temperature. It is now becoming possible, however, to begin studying the statistical mechanics and temperature related phase transitions of surfaces of solids. This is a completely new and unexplored area. As an example, the myriad of surface reconstructions that may exist on clean semiconductor surfaces at different temperatures is an extremely interesting and fundamental problem that needs to be investigated. Modern studies of phase transitions utilize a powerful theoretical tool which is the renormalization group scheme. The scheme is based on scaling ideas, and has as input simple spin Hamiltonians which model the degrees of freedom of the system. Until now there has been no way of calculating what these Hamiltonian parameters should be for real surfaces of solids. The total energy calculations described above, however, should provide precisely the kind of information needed. The exciting possiblity then arises of coupling the results of microscopic studies of surface systems (at zero temperature) with simple spin Hamiltonians and the renormalization group approach to study phase transitions at finite temperatures from "first principles."

In the past, using a simple semi-empirical total energy approach we succeeded in developing such a scheme and have applied it to the Si(100) surface, resolving impor-

tant questions regarding the structure of the Si(100) surface. We are investigating the possible phase transitions that may occur on the Ge(100) surface. This system, however, cannot be described accurately by a semi-empirical approach so that we are forced to use the more powerful and much more complex *ab-initio* total energy method discussed in section 10.1.

To perform these studies we have been developing a new scheme for relaxing a system with many degrees of freedom to its lowest energy configuration. The scheme is based on a molecular dynamics approach to calculating quantum mechanical total energies and resembles a simulated quench.

Using this approach we have calculated the total energy of various dimer models with either (2x1) or C(4x2) symmetry. The lowest energy dimer configuration for each rconstruction is shown in figure 10.3. We find, in particular, that the C(2x4) reconstruction is lower in energy that the (2x1) by 0.05 eV/dimer. The reason for this lies in the relaxation of the atoms in the second layer with respect to the dimers. Moreover, we find for the C(2x4) case that the energy surface is surprisingly flat for lateral displacements of the dimers along the surface. This should result in a distinct soft surface-phonon mode for the system.

At present we are performing total energy calculations on P(2x2) and C(2x2) reconstructions in order to have a large enough data-base to calculate a structural phase transistion termperature for Ge(100).
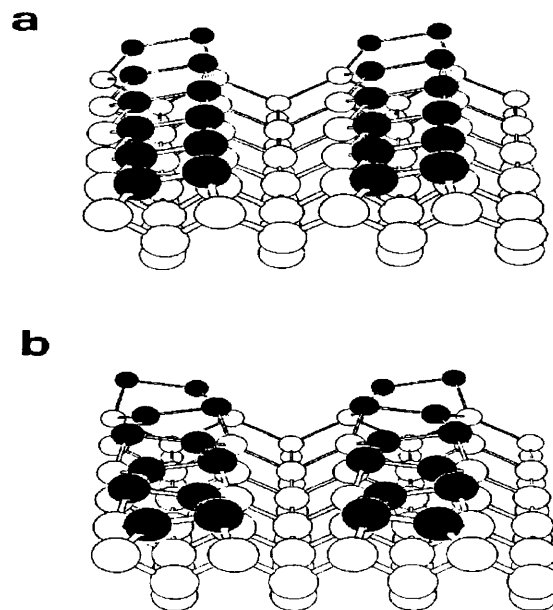


Figure 10.3. Perspective view of dimer models of the Ge(100) surface. The solid atoms are the surface layer. (a) Buckled (2x1) symmetry configuration. (b) Lowest- energy c (4x2)-symmetry dimer configuration obtained from our calculations.

# 10.3 Hydrogenation

The interaction of atomic hydrogen with cleaned semiconductor surfaces has been extensively studied for over a decade. Hydrogen atoms appear to saturate surface dangling bonds resulting in a nearly ideal, bulk-terminated plane of exposed surface atoms. It is interesting that in cases where the surface does not have the geometry and periodicity of the bulk-terminated plane, the interaction of hydrogen with surface atoms is strong enough to unreconstruct the complicated reconstruction patterns. This process takes place for example on the (2x1) Si(111) surface, which exhibits a low-energy $\pi$-bonded-chain reconstruction. Upon hydrogenation this chain of Si atoms with (2x1) periodicity reverts to the (1x1) pattern of the bulk-terminated plane. Similar phenomema have been observed on the Ge(111) surface. Theoretically, this process is not very well understood and a realistic, first-principles study with adequated accuracy to define precise low energy positions of atoms, corresponding total energies, and vibrational excitations above the ground state has been completely lacking.

Recently we have undertaken precisely such a study. Using *ab-initio* quantum mechanical total energy calculations, we find that the atomic positions of the hydrogenated Si and Ge(111) surfaces differ significantly from those of an ideal bulk terminated plane. In particular, the Si-H and Ge-H bonds are found to be considerably larger than the sum of covalent radii. The substrate relaxations are small and their physical origin can be explained in terms of electronic charge transfer which eliminates the surface dipole moment, by shifting charge from the hydrogen bond to the backbonds. This is very clearly illustrated for both Si(111):H and Ge(111):H by examining the total valence electron charge densities as shown in figure 10.4. As indicated in the third panel for each system, charge transfer drives the relaxations in order to cancel the dipole moment induced by the difference in electronegativity between H and Si(Ge).
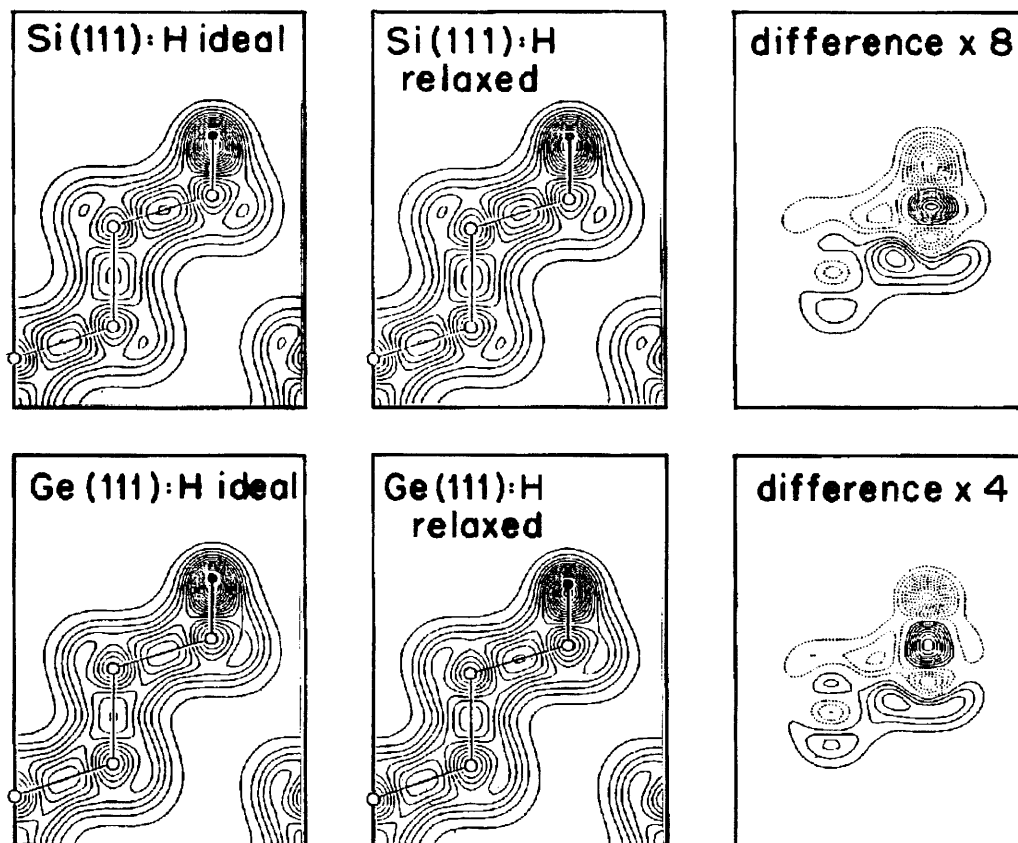
Figure 10.4. Valence charge density of Si(111):H and Ge(111):H plane. Open dots correspond to Si or Ge atoms and solid dots to H atoms. The difference between the ideal and fully relaxed configurations is given in the third panel for each case. Positive contours are shown in continuous lines, negative ones in dotted lines.