

10.0 Semiconductor Surface Studies

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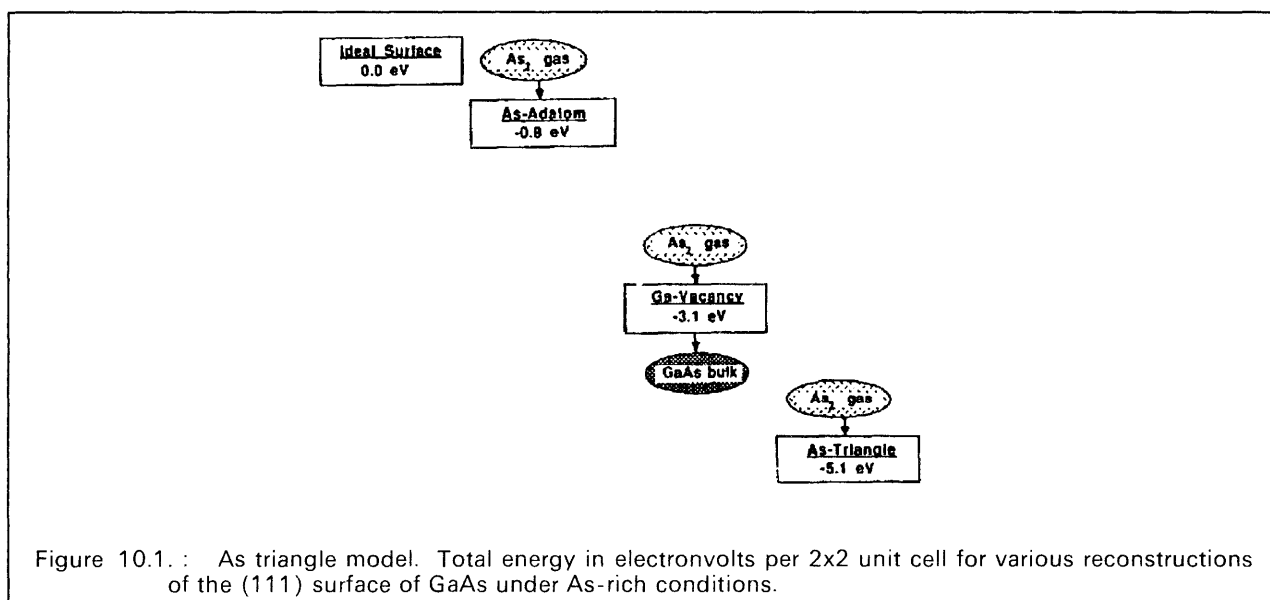
Understanding the properties of surfaces of solids and the interactions of atoms and molecules with surfaces has been of extreme importance both from technological and academic points of view. The recent advent of ultrahigh vacuum technology has made microscopic studies of well-characterized surface 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. 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 the “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 hydrogenation.

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.

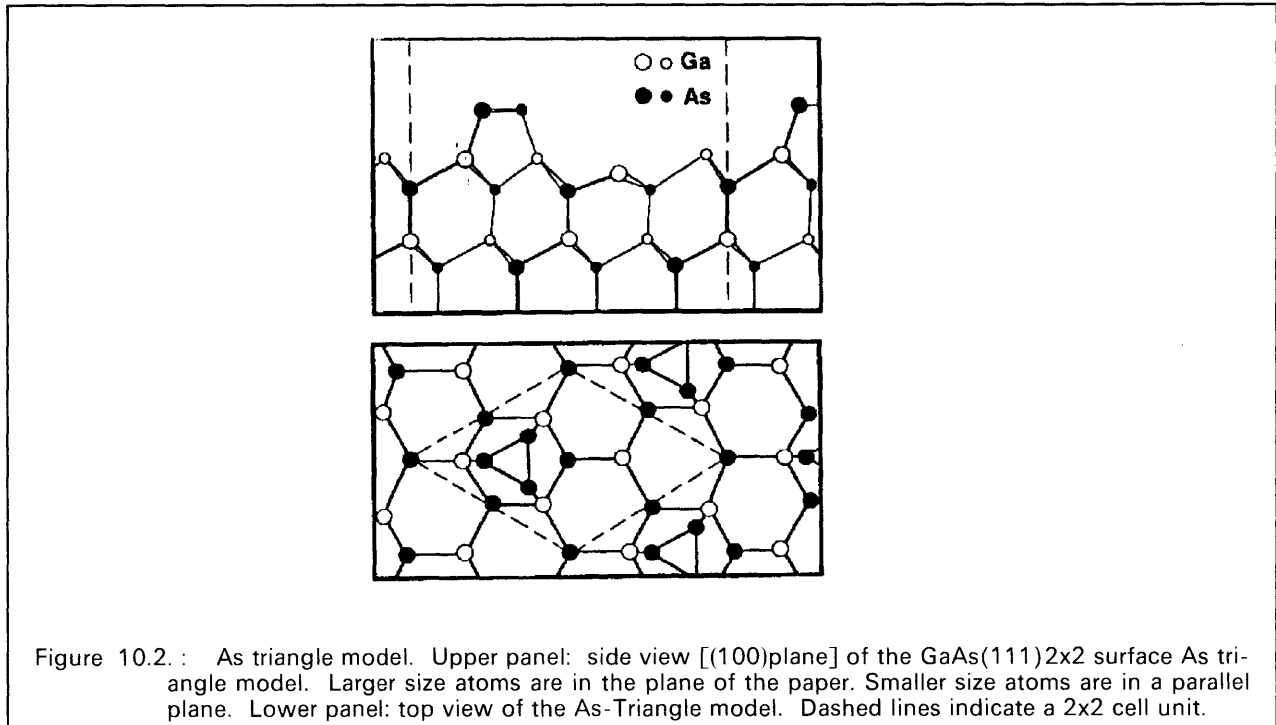
In recent years there has been considerable activity focused on determining the exact equilibrium geometry of the [111] surfaces of the III-V compounds. One of the most popular and intriguing models is the Ga/vacancy geometry where the removal of one out of four Ga atoms on the surface was believed to proceed exothermically and result in the lowest energy structure. For binary compound surface systems, however, it becomes meaningless to simply ask “What is the lowest energy surface geometry?” It is crucial to know the preparation conditions and the nature of the Ga and As reservoirs during the growth process. The relevant atomic reservoirs for the GaAs (111) surface are Ga-gas, As₂-gas, Ga-metal droplets and the GaAs-bulk. In Fig. 10.1 we illustrate the energies of several possible (2x2) reconstruction geometries we have studied, along with the corresponding reservoirs, relative to the ideal surface. We note that under As-rich conditions the lowest energy (2x2) reconstruction is a new model, the As-triangle geometry. This is shown in Fig. 10.2 and consists of three As adatoms bonded through As-As bonds which effectively compensate for the energy required to dissociate As₂ molecules which are the source of excess As atoms. Moreover, the triangle results in a nearly perfect geometric coordination of the remaining surface As and Ga atoms.



Finally, under Ga-rich conditions, we find that the Ga-vacancy geometry is indeed most favorable. Our results predict, then, that by varying the relative chemical potential of As and Ga, a phase transition should occur between the As-triangle and Ga-vacancy geometries. There are indirect experimental observations that appear to be consistent with this prediction.

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 phase transitions of surfaces of solids. This is a completely new and unex-



plored 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 possibility 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.”

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 important questions regarding the structure of the Si(100) surface. For example, we show that the (2x1) reconstruction geometry is not the ground state of the Si(100) surface and that higher order reconstructions can exist on the surface. In fact, it is found that two distinct families of reconstructed geometries (the “2x1” family and the “c(2x2)” family) can exist on the surface, with independent phase transitions occurring within each. Two critical transition temperatures are predicted representing order-disorder transitions. We are presently 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. Our calculations of the Ge(100) surface are currently underway.

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 π -bonded-chain reconstruction. Upon hydrogenation this chain of Si atoms with (2x1) periodicity reverts to the (1x1) pattern of the bulk-terminated plane. Similar phenomena have been observed on the Ge(111) surface. Theoretically, this process is not very well understood and a realistic, first-principles study with adequate accuracy to define precise low energy positions of atoms, corresponding total energies, and vibrational excitations above the ground state is completely lacking. Such a study is currently underway. Preliminary results, using *ab-initio* quantum mechanical total energy calculations, indicate that the atomic positions of the hydrogenated Si and Ge(111) surfaces differ significantly from those of an ideal bulk-terminated plane.