10. 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 the 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 are concentrated in three areas: (i) surface energy barriers, (ii) surface growth reaction pathways, and (iii) structural phase transitions and surface reconstruction geometries.

10.1 Surface Energy Barriers

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 is believed to proceed exothermically! Unfortunately, no realistic theoretical evaluation of such a model has been possible until now. The exciting possibility then arises of using our *ab–initio* total energy scheme to actually calculate the precise barrier for removing atoms from the surface. This would allow us to follow microscopically how an atom might escape from a surface. The results of our calculations are shown in Fig. 10–1.
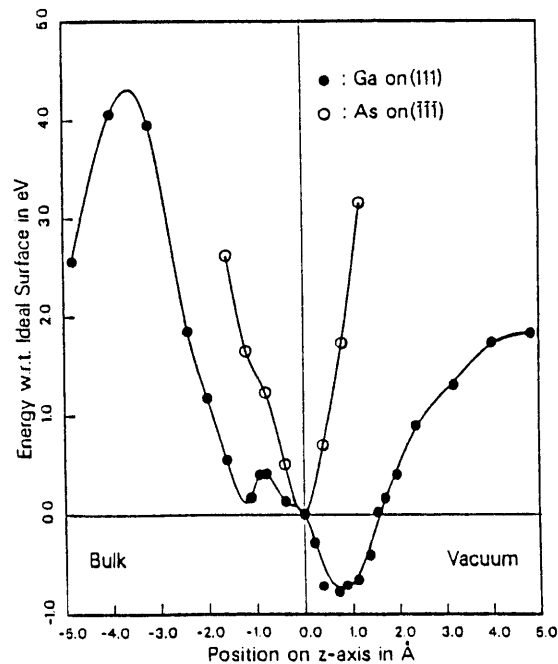
Figure 10-1: Relaxed surface total energy per 2x2 unit cell as a function of the position on the z–axis of the symmetry breaking atom.

Here we study the energetics of vacancy formation by gradually displacing Ga and As atoms on the (111) and ($\overline{1}\overline{1}\overline{1}$) surfaces of GaAs, respectively. Let us consider the (111) surface first. Vacancy formation can proceed by either removing one Ga atom per 2x2 unit cell into the vacuum or into the bulk. We note that as the Ga atoms are displaced toward the bulk, the energy essentially grows monotonically apart from a small glitch at $Z \approx -1.5$ Å . The vacancy geometry would certainly not be energetically favorable along this channel. If we displace the Ga atoms away from the surface, toward vacuum, the energy initially decreases significantly. However, it soon begins to rise rapidly resulting in an endothermic vacancy formation energy of 2.5eV. This is

in sharp contrast to the exothermic energies predicted from simple model estimates. We note that the lowest energy geometry would appear to be a buckled growing with $Z = 0.7$ Å . This is deceiving, however, as discussed in detail in the next section.

We conclude this section by noting that for the ($\bar{1}\bar{1}\bar{1}$) surface the energetics of As removal are completely different. It is quite clear that vacancy formation would be highly untenable.

10.2 Surface Reaction Channels

For binary compound surface systems 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, As_2-gas, Ga-metal droplets and GaAs-bulk. In Fig. 10–2 we illustrate the energies of a variety of possible 2x2 reconstruction geometries we have studied, along with the corresponding reservoirs relative to the ideal surface.

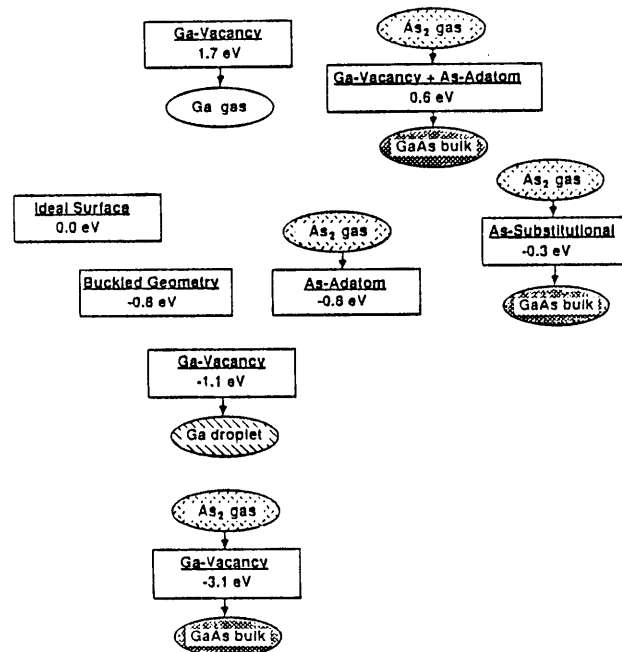Figure 10-2: Total energy per 2x2 unit cell of various reconstruction models for the (111) surface of GaAs.

For the vacancy model, removing the Ga atom to a Ga-gas reservoir is energetically unfavorable by 1.7eV. As described earlier, this corresponds to an endothermic removal energy of 2.5eV with respect to the buckled geometry. However, if the Ga-atom is placed in a Ga-metal droplet, vacancy formation can proceed exothermically! In fact, if excess As_2-gas is available, formation

of GaAs bulk pairs can lead to an even lower energy configuration. We note that the As-substitutional and As-adatom geometries do not compare favorably with the vacancy geometry. In fact, an interesting aspect of Fig. 10-2 is that it suggests that irrespective of experimental conditions (which lead to the presence of excess As or Ga atoms) the vacancy geometry has the lowest energy of all of the models proposed so far. A combination of the vacancy and adatom geometries is not favored because the respective relaxations oppose each other. We are currently investigating various reaction mechanisms appropriate for the ($\bar{1}$11) surface.

10.3 Structural Phase Transitions

Along a different direction, it is now possible to study the statistical mechanics and phase transitions of <u>real</u> 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 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. These calculations are currently underway.