

# 9. 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 have recently developed a method 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 two areas: i) chemisorption and ii) structural phase transitions and surface reconstruction geometries.

## 9.1 Chemisorption

Using "first principles" total energy calculations, it is possible to determine on a microscopic scale how atoms and molecules behave when they are placed 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 deposited atoms (or molecules) and the host atoms constituting the surface of the solid. These interactions can

strongly disturb the original atomic arrangement at the surface, can allow foreign atoms to stick only at particular positions on the surface, or can induce these atoms to move only along specific paths on the surface. The very exciting possibility then arises of actually calculating theoretically topographical atom-surface interaction energy maps, illustrating the various migration paths atoms might follow, as well as the places at which these atoms might like to bond. The result of the first "map" of this type is shown in Fig. 9-1.

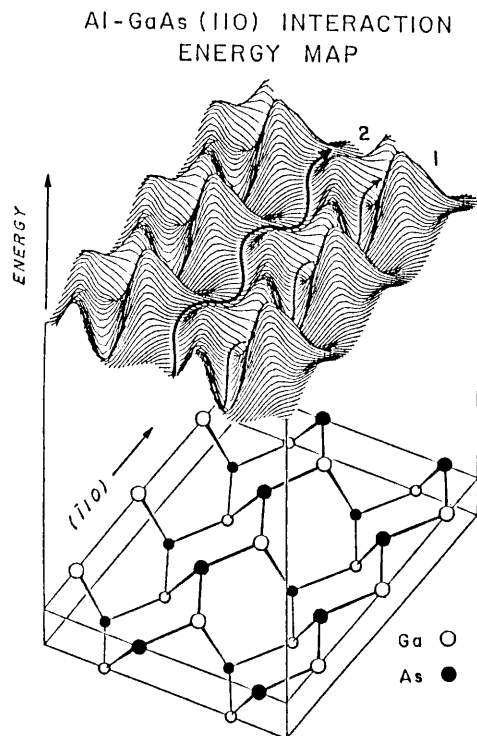
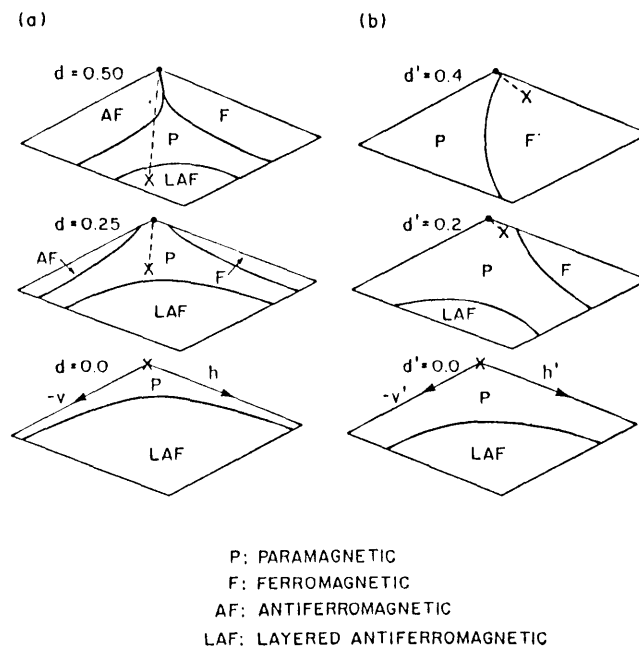


Figure 9-1: Interaction energy of Al with GaAs(110). The energy between the lowest dip and highest peak is  $\sim 1.5$  eV.

This represents the total interaction energy of an atom (Al) with a semiconductor surface (GaAs(110)) as a function of the position of the atom along the surface. The substrate atoms are allowed to relax in response to the presence of the Al atom. Several interesting features emerge. There is considerable structure across the surface, several metastable bonding sites can be identified, information about vibrational excitations is available, and two "easy" diffusion channels can be noted. The barriers along these channels are a couple of tenths of an eV. It is clear that diffusion is highly anisotropic occurring almost entirely along the (110) direction. A simple calculation also shows that at room temperature the Al atoms could easily move along these channels. It is then quite likely that adsorption of Al atoms at room temperature results in the formation of clusters or puddles on the GaAs surface. Calculations of this type can be a powerful theoretical tool in surface studies. They can help provide us with a realistic picture and a fundamental understanding of how atoms interact with surfaces.

## 9.2 Structural Phase Transitions

Along a different direction, it is now possible to study the statistical mechanics and phase transitions of real 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".



**Figure 9-2:** Phase diagrams in reduced parameter space for (a) "(2X1)" and (b) "c(2X2)" families. The "X"s correspond to intersections of a particular set of interaction parameters of the Si(100) system at varying temperatures. In (a) F is 2X1, LAF is p(2X2) and AF is c(4X2). In (b) F is c(2X2) and LAF is p(2X4). In each case, P denotes a disordered phase.

We have recently 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. A phase diagram for the Si(100) surface which can be used simultaneously for systems belonging to the same universality class such as Ge(100) and diamond (100) is shown in Fig. 9-2.