Chapter 2. Semiconductor Surface Studies

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2.1 Introduction

Sponsor

Understanding the properties of surfaces of solids and the interactions of atoms and molecules with surfaces has been of extreme importance both from the technological and academic points of view. The advent of ultrahigh vacuum technology has made microscopic studies of well-characterized surface systems possible. The way atoms move to reduce the energy of their 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 the properties of real surface systems. In particular, we are continuing our efforts in developing new techniques for calculating the total ground-state energy of a surface system from "first principles," so that we can provide accurate theoretical predictions of surface geometries and behavior. Our effort in this program have been concentrated in the areas of surface growth, surface reconstruction geometries, structural phase transitions, and chemisorption.

2.2 Flipping Dimers on the Si(100) Surface

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have revolutionized experimental studies of the properties of surfaces of solids. Both techniques utilize very sharp metallic tips (typically tungsten) to probe the surface and to obtain surface information at a resolution approaching the atomic scale. Apart from measuring fundamental properties of a surface, STM systems have also been suggested as platforms for the development of ultrahigh density information storage. However, building an ultrahigh density memory device using a scanning tip approach would require (1) a stable and controllable surface and (2) nondestructive interactions between the surface and tip. A *clean* surface may therefore prove to be more desirable than a partially adsorbed surface. In particular, a clean surface can provide a more stable, uniform, and dense distribution of surface storage elements. In addition, it may also be desirable to use the tip in a gentler mode as a mechanical tool rather than with a bias voltage pulse.

Thus to maximize the amount of information that could be stored, the ability to reversibly change data on the smallest scale possible and the robustness of the control over the atomic structure of the surface, it is of interest to search for a clean surface whose intrinsic surface atoms will be amenable to reversible displacements in a manner that is as benign to both tip and surface as possible. Such a task is extremely difficult to perform purely experimentally. Theoretical guidance in terms of accurate quantum-mechanical calculations would be a great benefit. Many microscopic processes are involved in the interactions of an atomically sharp tip and the atoms of the surface. Intimate contact between tip and surface can induce damage to the tip or the surface. This damage can occur because

of irreversible atomic rearrangements on the tip or surface, or atom transfers between tip and surface. What actually hapens will of course depend on how close the tip must approach the surface and, very importantly, on the identity of the tip and surface atoms which will determine the nature of bond formation and energetics. Therein lies the need for a realistic and accurate theoretical investigation.

In this work, we have undertaken such a theoretical investigation using state-of-the-art *ab-initio* density-functional conjugate gradients calculations. We have focused on the Si(100) surface because it is one of the very few surfaces known for which the surface atoms exist, intrinsically, in bistable configurations. Typical STM images of the Si(100) surface reveal that every two atoms on the outermost layer bond together to form a dimer and that these dimers lie side by side in rows running perpendicular to the dimer bonds. At room temperature, the dimers are predicted by theory to exist in fluctuating bistable (buckled dimer) configurations. At very low temperatures (e.g., liquid helium), the fluctuations of the dimers become frozen in and form alternating buckled-dimer rows. We wish to investigate whether it is possible to increase the interaction between the tip and a dimer so that the tip can flip a dimer and leave it flipped even after the tip has moved away. Moreover, can this be accomplished without damage to either tip or surface? The results of our calculations are displayed in figures 1 and 2. In each case, electronic charge densities associated with the valence electrons of the system are shown in a cross-sectional plane perpendicular to the (100) surface.

We first attempt to flip a dimer by moving the tip down onto the upper atom of the dimer and essentially pushing on it to induce a transition from one bistable configuration to the other one. This is illustrated in figure 1. As we proceed from the top panel to the bottom panel, the tip is moved down (from 2.5 Å above the surface to 2.25 to 2.0 to 1.75 Å) closer and closer to the surface, inducing the dimer to rotate, until the dimer reaches a horizontal configuration (at 2.0 Å), after which there occurs a discontinuous change in the equilibrium value of the dimer buckling angle (from 2 degrees to -24 degrees). At this point the dimer has flipped to its other buckled configuration. However, if we were to pull the tip back up, we would find that the tip drags the dimer back to its original configuration. This is a consequence of the rather strong covalent bond that is formed between the dimer atom and the edgemost tungsten atom of the tip. This bond can be seen as a small white region between the corresponding nuclei in figure 1.

Nevertheless, a dimer on the surface can be flipped so that it remains flipped even after the tip is
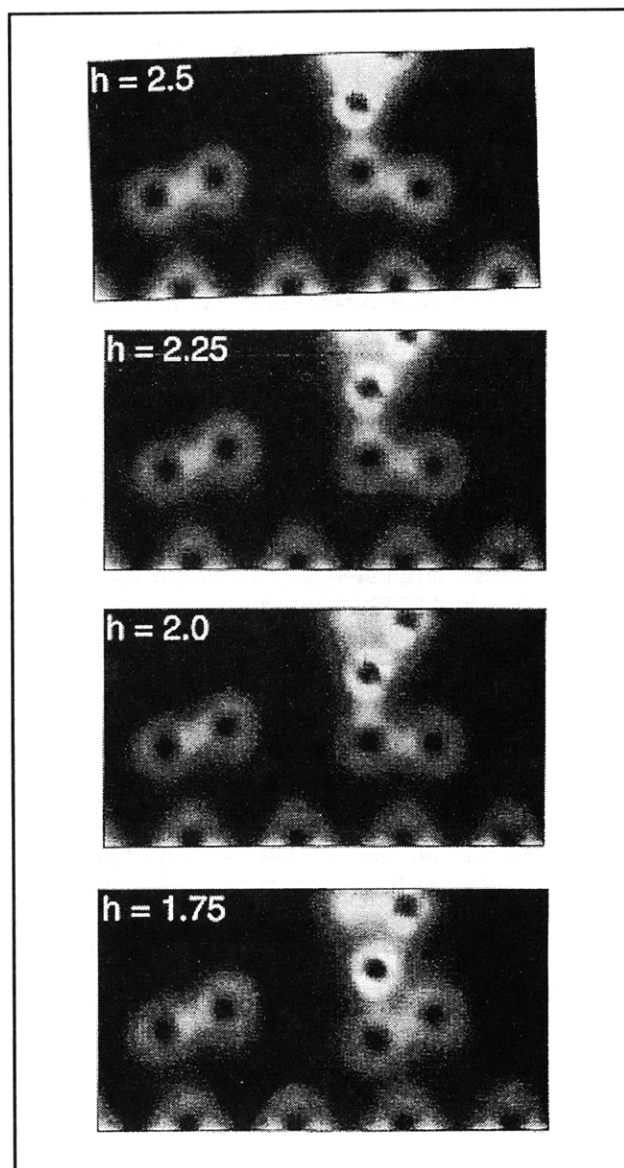

Figure 1. Sequence of the cross sections of the total valence electron charge density as the tip moves down from the top panel to the bottom panel. *h* measures the height of the tip from the surface.

removed by using the approach shown in figure 2. Since the tip-surface interaction is significant, the process of flipping is performed by having the tip pull on a dimer atom by forming a covalent bond between the tip atom and the lower dimer atom rather than push on the upper dimer atom. Proceeding from top to bottom, the first two panels represent a tip being brought down to a surface dimer (from 5.1 Å above the atom to 3.2 Å), while the next two panels correspond to the tip being pulled back up (to 3.95 and 5.2 Å). By bringing the tip down to the lower atom of a dimer, the tip can capture it by forming a covalent bond as before. A subsequent raising of the tip drags the dimer to its
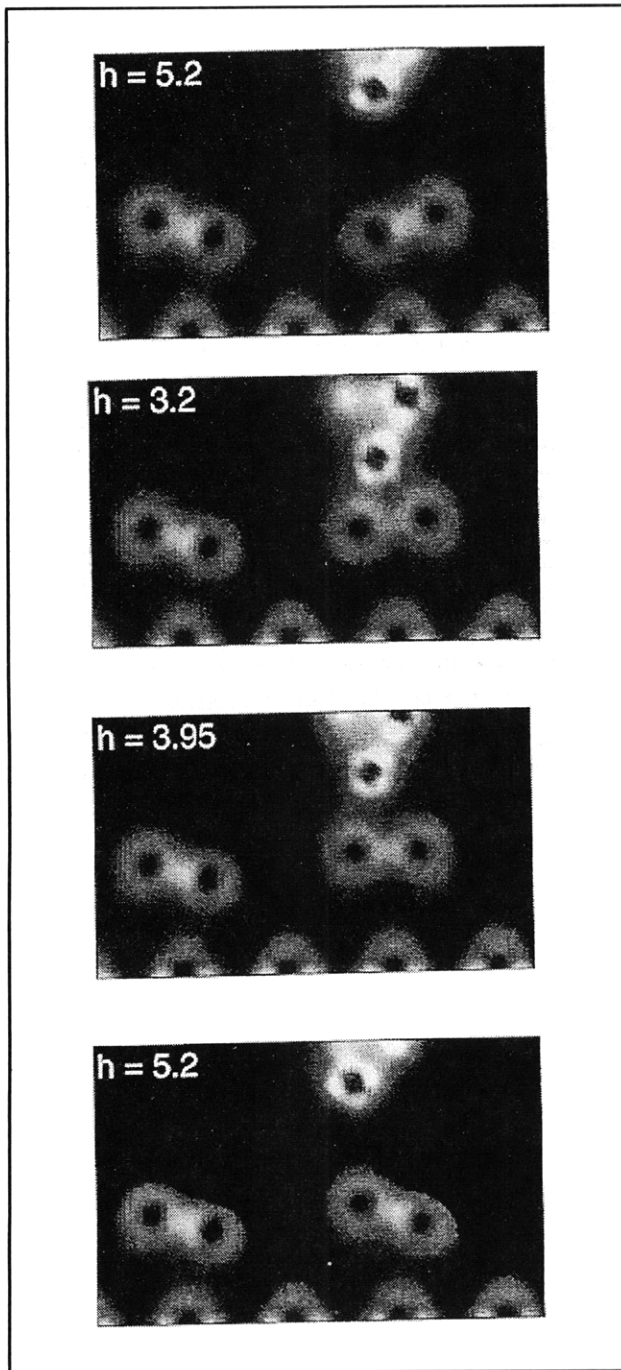
Figure 2. Sequence of the cross sections of the total valence electron charge density illustrating the plastic deformation process of the dimer. From the top panel to the second panel the tip is lowered to capture the dimer and the tip is brought up in the third panel and the bottom panel.

other buckled state. The bond between the tip and dimer eventually breaks without harming the dimer or the tip. This is because the silicon-tungsten bond between the tip and the dimer is weaker than both the silicon-silicon bonds in the dimer and the

tungsten-tungsten bonds in the tip. The net effect of this procedure is the flipping of a dimer on the surface that remains flipped after the tip is removed.

This predicted capability of the AFM or STM tip to rearrange atoms reversibly without damage to the system can be tested with current scanning microscope technology which provides control of the tip within 0.1 Å in the vertical direction and 1 Å in horizontal directions. Each of the steps explained in figure 2 can also be monitored by measuring the foce on the tip and comparing with the theoretical predictions.

Since each dimer on Si(100) can be made to exist in one of two possible buckled configurations, each dimer can conceivably store one bit of data of information. One simply assigns a 0 and a 1, respectively, to each dimer configuration. The recording of information would be accomplished by flipping dimers using the technique illustrated in figure 2. Information retrieval would be accomplished by simply performing a conventional STM or AFM horizontal scan at higher distance from the surface. This would enable one to image large portions of the surface swiftly without perturbing the existing dimer configurations. The entire intrinsic Si(100) surface now becomes a potentially massive storage bin. One bit of information for every dimer corresponds to one bit per 30 Å^2 or 420 Gbyte per mm^2. This corresponds to an increase by six orders of magnitude in storage capability compared to conventional devices.

2.3 Signatures of Bulk and Surface Defects

In this work, we have undertaken an exploration of the possibility of using STM (an intrinsically surface sensitive tool) to detect properties of bulk defects. The specific system we chose to investigate involves As antisite defects in the vicinity of the GaAs(110) surface.

The results of this work show how the predictive power of *ab initio* total energy methods can be used as an essential tool in the interpretation of such STM images. The interaction between defect and surface is expected to produce deviations from the bulk-like behavior. We find that these deviations are abruptly increased when the defect is located at the outermost surface plane. There is a striking difference in terms of total energies, level positions, and local electronic structure between fourfold coordinated (below the surface plane) and threefold coordinated (at the surface plane) defects, which allows us to unambiguously define them as *bulk*

and *surface* defects, respectively. We therefore can predict the conditions under which most of the STM-measured quantities will be faithful to the properties of the bulk defect. The presence of the surface, however, also produces nontrivial changes in the long-range electronic structure of bulk defects.

Table 1: Ab-initio total energies (in eV) for the antisite defect located at different distances below the surface.

Fourth layer	Third layer	Second layer	First layer
0.00	-0.15	-0.23	-2.07 (reference)

Table 1 shows total energy results for the arsenic antisite defect at the fourth layer, third layer, second layer, and first layer (surface layer) of GaAs(110). Notice the decrease in the total energy as the defect approaches the surface, which is indicative of an *attractive* defect-surface interaction. Moreover, notice the dramatic decrease in total energy as the antisite is moved from the second layer to the surface layer. This energy difference (about 1.8 eV) is too big to be explained in terms of "strain-release" effects solely. Therefore an abrupt change in the electronic structure of the defect must be occuring. The nature of this change is elucidated as we look at charge density contour plots for the occupied defect state in figure 3. In figure 3a (defect on the fourth layer), we see the familiar charge density signature of the bulk-like arsenic antisite defect, with s-like character on the central As atom and antibonding p-like character on the first neighboring As atoms (two of them are shown in the plane of the figure). In figures 3b and 3c (defects on the third and second layers, respectively), no significant change in the bulk-like charge density signature occurs. These three electronic states lie approximately at midgap, as the bulk defect does. In figure 3d, we display the charge density plot for the defect at the surface layer. It is clearly a resonant As dangling-bond state, and it lies well within the valence band (notice the mixing with valence band states). This abrupt change in the electronic structure is a direct consequence of the change from fourfold to threefold coordination as the defect is placed at the surface layer. As we shall describe more quantitatively in the next section, this change will produce remarkable effects in the spectroscopy properties of the defect.

Single electron energy level positions for the defect at different distances from the surface are displayed

in table 2. Notice that the level positions remain essentially bulk-like until the defect is located at the surface layer, when it then drops to abut 0.4 eV below the valence band edge. These results should have profound consequences as far as STM spectroscopy is concerned. They imply that it is indeed possible to obtain an accurate description of bulk defect energy levels using STM, as long as the defect is located below the surface layer. Furthermore, they predict that the surface defect will have very distinct spectroscopic signatures from the bulk ones.

Table 2: Single particle energy levels (in eV, with respect to the valence band edge) for the antisite defect located at different distances below the surface.

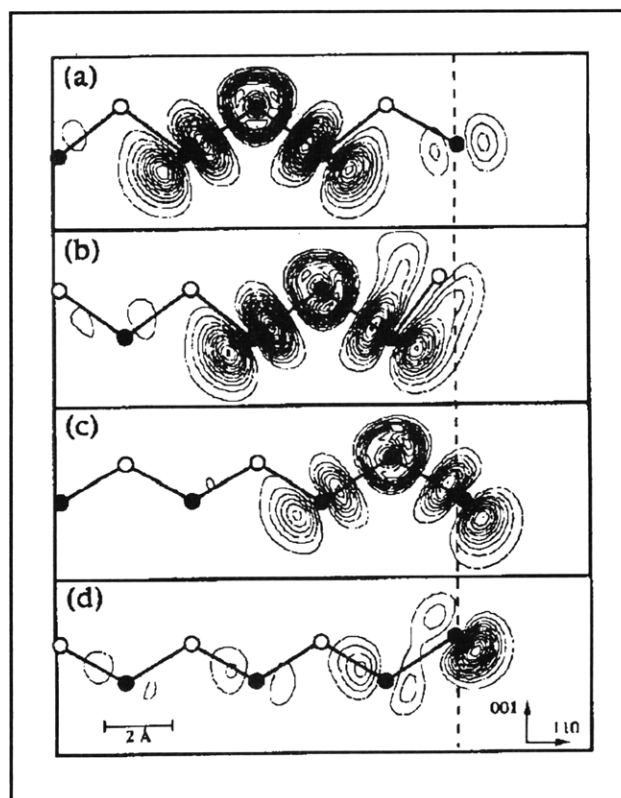| Bulk	Fourth layer	Third layer	Second layer	First layer
0.75 (fitted)	0.77	0.77	0.74	-0.39

Figure 3. Contour plots of electronic density for the antisite at the (a) fourth layer, (b) third layer, (c) second layer, and (d) first layer of the (110) surface. The dashed line denotes the position of the outermost As atoms in the pure surface. Black and white circles represent As and Ga atoms, respectively. Contours are evenly spaced by 0.005 electrons/Å³, running from 0.005 electron/Å³ to the maximum density in each case.

2.4 Publications

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