



# Chemical interactions in noncontact AFM on semiconductor surfaces: Si(111), Si(100) and GaAs(110)

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## Abstract

Total-energy pseudopotential calculations are used to study the imaging process in noncontact atomic force microscopy (AFM) on Si(111), Si(100) and GaAs(110) surfaces. The chemical bonding interaction between a localised dangling bond on the atom at the apex of the tip and the dangling bonds on the adatoms in the surface is shown to dominate the forces and the force gradients and, hence, to provide atomic resolution. The lateral resolution capabilities are tested in both the Si(100) and the GaAs(110) surfaces. In the first case, the two atoms in a dimer can be resolved due to the dimer flip induced by the interaction with the tip during the scan, while in the GaAs(110), we identify the anion sublattice as the one observed in the experimental images. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The achievement of true atomic resolution in atomic force microscopy (AFM) of well-characterized surfaces in ultra-high vacuum has been a long-standing goal in surface science. Experimental problems with controlling the repulsive forces at the apex atom resulting from the long-range attractive forces acting on the tip, and the limited understand-

ing of the complex nature of the surface–tip forces have made the progress unexpectedly slow. Recently Giessibl [1,2], Kitamura et al. [3], and Ueyama et al. [4] showed, for the first time, atomic resolution in the noncontact regime in UHV using a Si tip scanning a reactive surface, the reconstructed Si(111)  $7 \times 7$  surface. These experiments used a novel frequency modulation detection scheme that sensed the force gradient, instead of the force itself.

Since this pioneering work, several groups have imaged different surfaces (including Si(100)- $2 \times 1$  [5] and InP [6]) using the original *frequency shift*

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mode, have combined the force gradient detection with standard STM measurements [7,8], and have developed a new *amplitude damping* operation mode [9–11]. These experiments show that the technique is capable of achieving atomic resolution but they also motivate a number of questions concerning (1) the physical interaction responsible for the contrast, (2) the conditions for stable operation, (3) the quantitative relation between the force gradients and measured frequency shifts, (4) the relation between the quality of the images and the experimental conditions, and, more recently, (5) the origin of the discontinuities observed in the force gradient curve [11].

As the resolution of any scanning probe microscope relies on the variation of the signal that is used to obtain the image, we expect that a careful theoretical analysis of the tip-sample forces could shed light on some of these issues. In particular, the atomic resolution observed challenges the common understanding that only long-range Van der Waals (VdW) interactions are present in the noncontact regime. Quantum mechanical simulations, where the forces acting between different tips and the surface are accurately described, have recently shown [12] that another contrast mechanism, the interaction between dangling bonds of adatoms in the surface and a dangling bond pointing out of the apex atom of the tip, play an important role in the quality of the images obtained in noncontact AFM. We showed that, even for distances as large as  $\sim 5 \text{ \AA}$ , which was the estimated distance of closest approach in the earlier experiments, this covalent chemical interaction generates forces which are of comparable magnitude to the VdW tip–surface interaction, dominates the force gradients, and presents significant variations when the tip is scanned across the surface. Hence, it is this interaction that provides a mechanism for atomic resolution imaging of reactive surfaces. Since then, extensive simulations [13]—including displacement curves over several points of the unit cell and lateral scans over a large area of the surface unit cell—have been used to completely characterize that covalent interaction for the case of the Si(111)- $7 \times 7$  reconstruction.

The aim of this paper is two-fold. First, we present our results for the force and force gradients on the Si(111) surface, compare the contributions of the chemical covalent interaction and VdW, and

discuss the role of atomic relaxation in the tip and the surface, and the possible parameterization of the tip–surface interaction using model potentials. Our main findings will help to understand a number of experimental issues raised above, such as the relation between the quality of the images and the experimental conditions, with special emphasis on the role of the tip preparation, and the origin of the recently observed discontinuities in the force gradient curve. Secondly, we test the limits of the lateral resolution in NCAFM. We analyze the Si(100)- $c(4 \times 2)$  reconstruction, where the resolution of the two atoms in the dimers poses a challenging problem, and briefly present our results for the GaAs(110) system [14], where experimental images for this and other III–V semiconductors like InP, fail to resolve the two sublattices present on the surface.

## 2. Simulation of the operation of the microscope

We have performed direct simulations of the interaction of different tips scanning on Si(111)- $5 \times 5$ , which is the smallest model containing all the basic structural features of the Si(111)- $7 \times 7$  reconstruction, the Si(100)- $c(4 \times 2)$  and the GaAs(110)- $1 \times 1$  reconstructions. Each system is modelled using a supercell with inversion symmetry containing a slab for the corresponding reconstruction, two tips (one on each side of the Si slab) and a vacuum region. Sharp tetrahedral tips with four (10) Si atoms stacked in two (three) Si(111) planes have been considered to model the etched Si tips used in the experiment. The dangling bonds of the Si atoms in the base of the tips are saturated with hydrogens. As shown elsewhere [12,13], these two tips provide similar results and only the four Si tip will be used in the calculations for the Si(100) and GaAs(110) surfaces.

The operation of the microscope was simulated in a stepwise, quasi-static manner by making small movements of the rigid part of the tip (the Si atoms in the base of the tip and the H atoms attached to them) parallel to the slab in the lateral scans, and perpendicular to the surface in the displacement curves. At each step the atoms in both the slab and the tip were allowed to relax to their equilibrium positions for that particular position of the tip until the total energy was converged to within less than

$5 \times 10^{-5}$  eV per atom, and the forces in the atoms to less than  $0.01$  eV/Å.

Massively parallel computing, coupled with improved algorithms for the implementation of total-energy pseudopotential calculations and the new gradient approximations for the exchange correlation functional were employed to perform our quantum mechanical simulations (for the technical details see Ref. [13]).

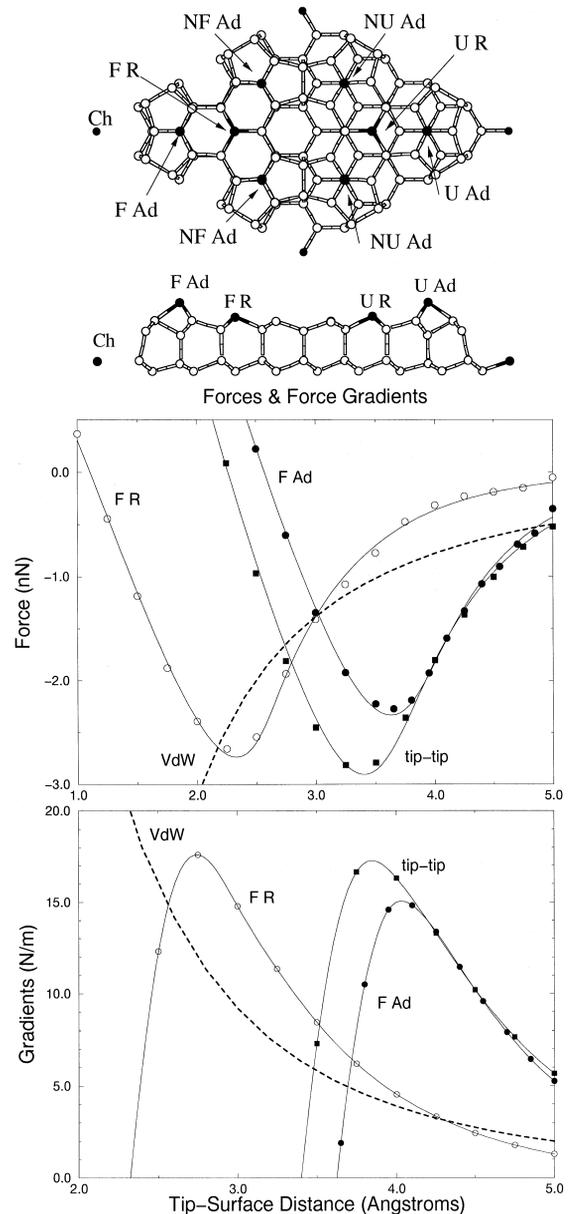
### 3. Results

#### 3.1. Si(111)5 × 5

Fig. 1 summarizes the results for the Si(111)-5 × 5 reconstruction. Normal forces and force gradients for the 10 atom Si tip scanning on top of one of the adatoms and a rest atom on the faulted half of the unit cell are compared to the results for the long-range (VdW) interaction for a Si tip with a radius of  $40$  Å (see Ref. [13] for details on the VdW calculation), and the chemical interaction of a model system consisting of two interacting Si tips. All the results are plotted as a function of the ‘tip–surface distance,’ which is defined as the difference in height between the unrelaxed tip apex and the highest adatom in the unrelaxed surface. With these definitions, variations in the tip–surface distance are then directly related to the relative displacements of tip and sample which are measured in the experiments. Force gradients are determined as derivatives of the force fits as explained below.

Fig. 1. Normal force (medium panel) and force gradients (lower panel) for the tip–diagonal adatom (black circles), the tip–rest atom (white circles), and the tip–tip (squares) interaction. In the case of the force the symbols correspond to the calculated values of the force while the lines represent the Morse fit. The gradients are obtained as a derivative of the corresponding force fits. Forces and force gradients associated with the long-range VdW interaction for a macroscopic spherical tip of radius  $40$  Å are indicated by dashed lines. The top panel shows a ball-and-stick model of the  $5 \times 5$  reconstruction, including a top view of the unit cell and a lateral view of the atoms close to the lattice plane along the long diagonal. The atoms with dangling bonds are marked: corner hole (Ch), faulted (F R) and unfaulted (U R) rest atoms, faulted diagonal (F Ad) and off-diagonal (NF Ad) adatoms, and unfaulted diagonal (U Ad) and off-diagonal (NU Ad) adatoms.

This figure clearly shows the similarities between all the covalent bonding interactions as opposed to the VdW interaction, and provides clear evidence of the fact that covalent bonding dominates the interaction which cause the frequency shifts used to create the experimental images. A natural conclusion which emerges from the data is that only the short-range



interaction at ‘near contact’ distances ( $\sim 3\text{--}5 \text{ \AA}$ ) is able to provide a variation in the forces and force gradients across the surface which is large enough to achieve atomic resolution. This short-range interaction is essentially an interaction between the surface adatom dangling bond and tip apex dangling bond. This can be seen by comparing the curves for the scans over an adatom, a rest atom and for the model system consisting of two interacting Si tips. The differences in the position of the minima between the adatom curve and the two tips can be understood by considering that when the atoms in the tip and the surface are allowed to relax under the forces present, the relative movement of the tip apex and the surface atoms is no longer the same as that of more distant parts of the tip and the sample. This effect, already relevant for a tip–surface distance of  $5 \text{ \AA}$ , where the actual apex–adatom distance (apex–apex distance for the two interacting tips) after atomic relaxation reduces to  $4.72 \text{ \AA}$  and  $4.92 \text{ \AA}$  for the two Si tips, becomes increasingly important as the tip and surface get closer. A detailed discussion of the behaviour of apex–surface distance as a function of the tip displacement can be found in Ref. [13]. Differences between the curves thus reflect the different atomic relaxations due to the different bonding of the atoms to the surface in the various systems considered. In all the cases the minimum in the total energy (zero in the normal force curves shown in Fig. 1) corresponds to the tip position where the apex–surface atom distance (apex–apex distance) is roughly equal to  $2.35 \text{ \AA}$ , the Si–Si nearest neighbour distance in bulk Si. The vertical scan over the rest atom shows similar behaviour to the scan over the adatom but the minima in the normal force is displaced by around  $1.25 \text{ \AA}$ , which is roughly the difference in height ( $1.12 \text{ \AA}$ ) between the adatom and rest atom in the  $5 \times 5$  reconstruction. The zero force point (minimum in the total energy) also corresponds to a distance between the tip apex atom and the rest atom equal to  $2.35 \text{ \AA}$ . Almost identical results are obtained for the scans on atoms on the unfaulted [13].

In order to perform simulations of the cantilever dynamics under the conditions used in noncontact AFM it would be desirable to have a simple but accurate description of the tip–surface interaction. Morse potentials provide a reasonable description of

covalent bonding in a diatomic molecule through the simple analytical function:

$$V(r) = V_0 \left[ \left( 1 - \exp \left[ -2b \frac{r - R_c}{R_c} \right] \right)^2 - 1 \right], \quad (1)$$

where  $V(r)$  represents the total bonding energy as a function of the interatomic distance  $r$ , and  $V_0$ ,  $b$  and  $R_c$  are parameters which define the strength and range of the bonding interaction.

Fits to the calculated tip–adatom, tip–rest atom, and tip–tip forces using the derivative of the Morse potential and taking  $r$  as the real apex–surface atom distance, are shown in Fig. 1. It should be noticed that although the fit is done with the real interatomic distance, the plot is presented with respect to the corresponding tip–surface distance defined above. Typical values for the parameters from the tip–adatom force are:  $V_0 = 2.273 \text{ eV}$ ,  $b = 1.497$  and  $R_c = 2.357 \text{ \AA}$ . These fits reproduce the behaviour of the force close to its minimum, and the integration of those curves provide a reasonable, although not very accurate, description of the total energy for the different systems. The quality of the fits deteriorates if we try to include more fitting points in the repulsive part of the force, showing that, as one can expect, the tip–surface interaction deviates from the pure ‘diatomic’ case as the tip approaches the surface and the response of the adatom or the rest atom becomes influenced by the atoms in the layers below. It should be noted that good fits are only obtained when we use the real apex–surface atom distance, further confirming the importance of the relaxation effects described above.

The main finding from the results above is that the attractive chemical interaction between dangling bonds operating at ‘near contact’ distances has a strong dependence on the tip–surface distance and provides a clear contrast among different sites of the unit cell. The available experimental evidence supports this conclusion. The contrast observed in the constant frequency shift images [1–4,7,8], where maxima in the tip height occur at the position of the adatoms, correlates with the maxima in normal force and gradients on top of the adatoms obtained in our simulations. Further support comes from the experimental observation that the onset of tunneling current and the rapid variation of frequency shift occur

simultaneously, and from the discontinuities observed in some of the frequency shift curves [6,11], that can be explained in terms of the onset of a chemical bonding interaction.

More importantly, these results indicate that there should be a strong correlation between the tip preparation and the quality of the images. This is actually what the experiments show: the discontinuities in the force gradient curves only appear after accidental contact between the tip and the surface. The atomic resolution images on the Si(110) are only obtained after the Au coating on the tip is removed due to a crash with the surface.

It can be argued that although the chemical interaction dominates the force gradients, its short range nature precludes a large contribution to the measured frequency shift when compared with other smaller but long range interactions such as VdW. However, the recent perturbative analysis by Giessibl [15] shows that the chemical forces have a pronounced effect on the frequency shift at near contact distances.

### 3.2. Si(100)-c(4 × 2)

The imaging of the Si(100)-c(4 × 2) poses a challenge to noncontact AFM as the distance between the atoms in the dimers (2.34 Å, very close to the nearest neighbour distance in bulk Si) is much smaller than the adatom distance in the Si(111)-5 × 5. We have determined the total energy and normal force as a function of the tip–surface distance for two different positions of the tip, close to each of the atoms in one of the dimers. They show a similar behaviour to the results found for the Si(111) surface (details will be discussed elsewhere), with the atoms on the surface displacing laterally in order to maximize the overlap with the tip dangling bond (Notice that in this case the unsaturated dangling bonds are not pointing perpendicular to the surface as in the Si(111) case). More importantly, the displacement curve close to the lower atom in the dimer indicates that the tip can induce the flip of the dimer at a distance around 3.5–3.75 Å. It should be noticed that the presence of the tip is already reducing the barrier for the dimer flip for larger distances than the one quoted above

where that barrier goes to zero and spontaneous flip can occur.

Lateral scans at a constant tip height along the dimer bond direction have been performed at two different tip–surface distances: 4 and 5 Å. The tip–surface distance refers to the difference in the normal coordinate of the apex atom and the upper atom in one of the dimers. The tip lateral displacement in each step is 0.5 Å. Fig. 2 shows the normal force for these two scans, starting from a position where the tip is on top of the upper atom in one of the dimers (position labelled (A) in the graph). The tip scans from left to right in the figure and the labels A–D correspond to the tip positions where the tip is closer to one of the atoms in the dimers during the scan. Fig. 2 also includes a ball-and-stick representation of the initial configuration of the atoms close to the scan line. The scan at 5 Å presents a small contrast and, due to the difference in height between the atoms in a dimer (0.62 Å in our calculation), only the upper atoms in the dimers can be imaged.

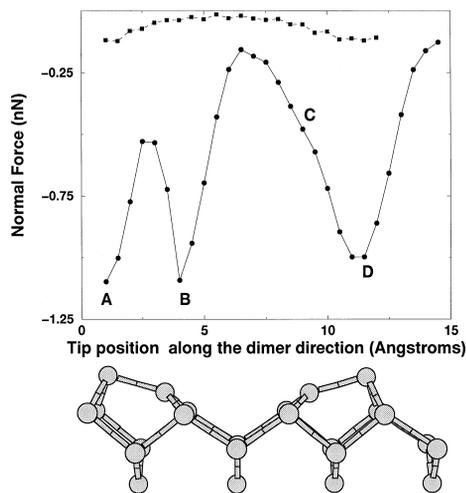


Fig. 2. Normal force for a lateral scan along the dimer bond direction at two different tip heights: 5 Å (squares) and 4 Å (circles) above the upper atom in the dimers. The labels A–D correspond to the positions where the tip is close to one of the atoms in the dimers during the scan. The scan proceeds from A to D. A lateral view of the atoms close to the scan direction in their initial configuration is also shown. The differences observed for the lower atom in the two dimers (positions B and C) in the 4 Å scan are due to the flip of the dimer on the left induced by the interaction with the tip. Only the dimers where the tip scans first over the upper atom are flipped (see text).

The situation changes significantly in the scan at 4 Å where the tip induces the flip of one of the dimers, and the originally lower atom in that dimer moves up and can be clearly imaged (position labelled B in Fig. 2). Notice that as the flip is an activated process, the dimer remains in the new buckling configuration as the tip continues the scan. In the 4 Å scan there is a clear contrast for the upper atoms in the dimers positions A and D, but the height difference still prevents the imaging of the lower atoms, except for the case where the dimer flips position B. It has been shown in the case of a tungsten tip on the same surface [16] that the barrier for the flip decreases significantly when the tip is placed directly above the dimer bond. According to that calculation, one can expect that both dimers should flip during the scan. Our calculations show that the orientation of the dimer with respect to the scan direction, not taken into account in that static calculation, play a role in the process: the dimer flips only in the case where the tip scans first over the upper atom. Only in this case, the displacement of the upper atom, which tries to follow the tip during the scan, pushes the lower atom up, further lowering the barrier for the flip. The comparison of the results for the two dimers scanned indicates that the lateral resolution is clearly enhanced by the flip of the dimer. This enhancement is related to the simultaneous displacement of the atoms in the dimer, with the upper atom moving down and so reducing the interaction, and the lower atom moving up and increasing significantly the force on the tip. It is important to notice that the maximum of the force occurs slightly off the position on top of the dimer atoms (0.3 Å in the case of position B), as one can expect from the orientation of the corresponding dangling bonds. A similar effect is observed in the STM images of (110) surfaces of III–V compounds [17]. Due to this effect and the changes in the atom positions due to the flip of the dimer, the apparent distance between the atoms in the dimer which will be observed in the image is approximately 3 Å.

From the comparison of the scans at 4 and 5 Å, we would expect that the noncontact AFM images taken at large frequency shift, where the tip is closer to the surface, will show, even for temperatures below RT, symmetric dimers where the two atoms in the dimer are clearly resolved, similarly to what is

observed in the empty state STM images of this surface at RT. This is indeed what the results of Kitamura and Iwatsuki [5] show in the images obtained with a tip where the original Au coating has been removed in a crash with the surface, confirming again the important role of tip preparation to improve the resolution of the images.

### 3.3. GaAs(110)

The InP(110) images obtained by Sugawara et al. [6] only show a rectangular cell periodicity, with no traces of the zig-zag chains characteristic of this surface. These maxima have been naturally attributed to one of the sublattice present in the surface. Experiments on the GaAs(110) surface show similar results [18]. We have performed both displacement curves and lateral scans at constant height along different directions on the GaAs(110) surface [14]. The displacement curves show an important counter relaxation of the Ga atoms for tip–surface distances around 3.5 Å. Our results for the lateral scans indicate that for tip–surface distances greater than 4 Å only the anion sublattice can be imaged. For distances between 3 and 4 Å both maxima close to the Ga atoms and at intermediate positions, due to the interaction of the tip with neighbouring As atoms, are observed.

## 4. Conclusions

Quantum mechanical simulations provide a unique tool to characterize the tip–surface interaction in the noncontact AFM operation. The chemical interaction between dangling bonds in the tip and surface has been shown to dominate the forces and force gradients and to provide atomic resolution in the near contact region. This result stresses the importance of the tip preparation in order to improve the quality of the images. The lateral resolution capabilities have been tested in both the Si(100) and the GaAs(110) surfaces. In the first case, the two atoms in a dimer can be resolved due to the dimer flip induced by the interaction with the tip during the scan, while in the GaAs(110), we identify the anion sublattice as the one observed in the experimental images.

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