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Contrast mechanism in non-contact AFM on reactive surfaces

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Abstract

Total-energy pseudopotential calculations are used to study the imaging process in non-contact atomic force microscopy on Si(111) surfaces. The atomic resolution seen in the experiments is attributed to the onset of covalent bonding between a localised dangling bond on the atom at the apex of the tip and the dangling bonds on the adatoms in the surface. This interaction dominates the force gradients, which drive the frequency changes used to create the experimental images. Force vs. tip displacement curves provide information about the optimum operation range and show the importance of the relaxation of the tip apex and surface atoms in the understanding of the damping images. © 1998 Elsevier Science B.V.

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1. Introduction

The atomic force microscope (AFM) [1] was developed as a tool capable of resolving surface structures of both conductors and insulators by probing the spatial variation of the interatomic forces between a tip and a surface. However, progress towards true atomic resolution in atomic force microscopy in ultrahigh vacuum has been slower than in scanning tunneling microscopy (STM). Operation in the contact regime, where tip and sample are in close mechanical contact, is affected by friction and local deformations of the surface which distort the images in an uncontrolled way. On the other hand, the measurement of the weak forces required for atomic resolution in the non-contact attractive regime is a challenging experimental problem.

Giessibl [2,3] and Kitamura and Iwatsuki [4] showed, for the first time, atomic resolution in the non-contact [UHV] regime using a Si tip scanning a reactive surface, the reconstructed Si(111) 7×7 surface. These experiments used a novel frequency modulation detection scheme [5] that sensed the force gradient, instead of the force itself.

A quick comparison of the AFM images in Refs. [2–4] with the STM images of the same surface showed that we were still far from an equivalent performance. Giessibl's experiment showed a low-quality image of the surface, similar to Kitamura and Iwatsuki's result, except for a small area where suddenly, for the width of a unit cell, the characteristic protrusions associated with the 12 adatoms on the top layer of the reconstruction could be clearly seen.

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After this, the resolution deteriorated again, and no image was obtained for the rest of the scan.

The resolution of any scanning probe microscope relies on the variation of the signal that is used to obtain the image. The atomic resolution observed in the experiments cited above challenge the common understanding that only long range Van der Waals (VdW) interactions are present in the non-contact regime. Quantum mechanical simulations, where the forces acting between different tips and the surface are accurately described, have recently shown [6] that another contrast mechanism, the interaction between the dangling bonds on the adatoms in the surface and a dangling bond pointing out of the apex atom of the tip, dominates at the distance of closest approach. This covalent chemical interaction provides a mechanism for atomic resolution imaging and suggests an explanation for the variations in resolution observed in terms of structural changes which ocurred in the tip during the scanning process. Recent experimental results [7–9] on the same Si(111) 7 × 7 surface have shown the crucial role of the tip treatment to achieve atomic resolution, giving support to the contrast mechanism proposed above.

The aim of this paper is to present a detailed description of the tip–sample interaction based on our simulations and to compare it to the recent experimental evidence. Results for the lateral scans with different tips on Si(111) surfaces will provide clear evidence of the central role of dangling bond interaction in the imaging of reactive surfaces and explain the results obtained in the frequency shift measurements. Total-energy and force curves during tip–sample approach (displacement curves), taken at different positions over the surface unit cell, will contribute to the determination of the optimum operation parameters for the constant frequency shift images and the understanding of the new constant damping images [9,10].

2. Formalism

2.1. Simulation of the operation of the microscope

We have performed direct simulations of the interaction of different tips scanning on Si(111)-5 × 5 reconstruction, which is the smallest model containing all the basic structural features of the Si(111)-7 × 7 reconstruction, in particular adatoms in the top layer with unsaturated bonds (dangling bonds) pointing out of the surface. The system is modelled using a supercell with inversion symmetry containing a 200 (72) atom Si(111) slab for the 5 × 5 (3 × 3) reconstruction, two tips (one on each side of the Si slab) and a vacuum region. Sharp tetrahedral tips with 4 (10) Si atoms stacked in two (three) Si(111) planes have been considered to model the etched Si tips used in the experiment. We have saturated the dangling bonds of the atoms in the base of these tips with hydrogen atoms, except in one case for reasons to be discussed below.

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 at a constant height above the surface. 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 5×10^{-5} eV per atom, and the forces in the atoms to less than 0.01 eV/Å. Finite temperature effects are not going to modify substantially our results since typical atomic frequencies are much larger than the tip oscillation frequency.

2.2. Method of calculation

Massively parallel computing, coupled with improved algorithms for the implementation of total-energy pseudopotential calculations [11] and the new gradient approximations for the exchange correlation functional [12] were employed to perform our quantum mechanical simulations. Optimized non-local pseudopotentials [13], applied in the Kleinman–Bylander form [14], were used. The electronic states were expanded at the Γ point of the Brillouin zone. A cutoff for the plane wave basis set of 7 Ry was used. The Γ sampling provides a good description of both total energies and vibrational frequencies for the 5 × 5 reconstruction [15]. In the case of the smaller 3 × 3 reconstruction a better sampling, with three $\boldsymbol{k}$ points, has been used. Extensive checks [6] show that our results are not significantly affected by the limited cutoff energy and $\boldsymbol{k}$ point sampling used in the calculations.

3. Results

3.1. Lateral scans

Our aim is to explore other contrast mechanisms in addition to the Van der Waals interaction, in particular the interaction between the dangling bonds in the adatoms and a dangling bond pointing out of the apex atom of the tip. In order to analyze this interaction, we have simulated scans along the long diagonal of the 5×5 unit cell using three different tips. Two of the tips have four Si atoms arranged in the same tetrahedral structure, the only difference being the presence or absence of H atoms saturating the dangling bonds of the atoms in the base of the tip. This saturation changes the hybridization of the Si atoms in the tip to a state close to the sp^3 of the bulk, leaving the apex atom with a dangling bond directed towards the surface. The third tip, with 10 Si atoms and H saturating the base, has a charge distribution in the apex similar to the four atom tip saturated with H.

Fig. 1 shows the total energy [1] and the normal force for the two 4 Si atom tips scanning across one of the adatoms and a complete scan along the long diagonal of the 5×5 unit cell with the 10 Si atom tip at a constant height of 5 Å, the estimated distance of closest approach in the experiments. All the tips show minima in the total energy at the position of the adatoms, but the minima are much deeper for the tips which have dangling bonds pointing towards the surface. Similar results are obtained for the normal force, with a clear enhancement of the contrast (the rest atoms can be clearly resolved with the normal force). Comparing the results for the tips with 4 and 10 Si atoms it is clear that the tip–surface interaction is completely dominated by the dangling bond of the apex atom.

The results described above indicate the onset of covalent bonding between the dangling bonds in the adatoms and the apex atom of the tip. Clear evidence of this bonding process comes from the normal displacements of the adatoms (see Fig. 1) and the

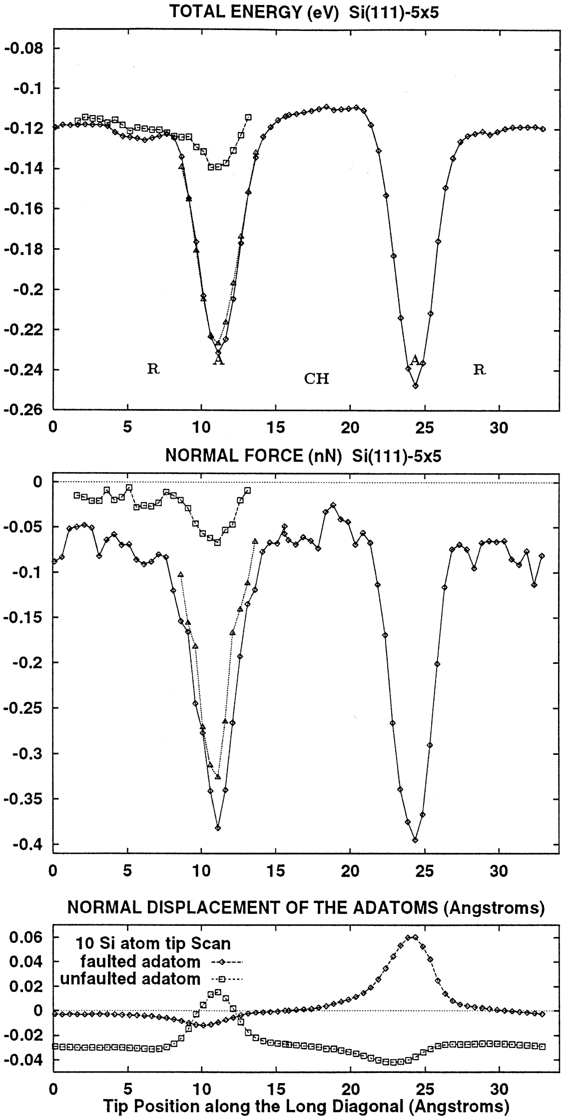

Fig. 1. Total energy (in eV) and normal force (in nN) for the two 4 Si atom tips scanning across one of the adatoms and a complete scan along the long diagonal of the 5×5 unit cell with the 10 Si atom tip at a constant height of 5 Å. Squares correspond to the 4 Si atom tip without a dangling bond, triangles (diamonds) to the 4 (10) Si atom tip where the tip base has been saturated with H and a dangling bond directed towards the surface appears at the tip apex. The position of the atoms with dangling bonds along the long diagonal is marked: adatoms (A), rest atoms (R) and corner hole (CH). The faulted half of the unit cell is on the right of the image. Notice that all the tips show minima in the energy and the forces at the position of the adatom, with a larger contrast for the tips with a dangling bond. The normal displacement of the adatoms during the complete scan with the 10 Si atom tip is also included: squares (diamonds) correspond to the adatom in the unfaulted (faulted) half of the cell.

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[1] The zero corresponds to the sum of the total energy calculated independently for the slab and the tip using the same unit cell.

Table 1
Comparison of the relative contribution of the covalent bonding interaction and the tip–surface Van der Waals interaction to the normal force and force gradient for a normal distance of 5 Å

	Force	Gradient
Microscopic VdW	−0.02 nN	0.15 N/m
Spherical ($R = 40$) VdW	−0.50 nN	2 N/m
Tip without DB	−0.07 nN	2 N/m
Tip with DB	−0.39 nN	10–12 N/m

The VdW values correspond to the 4 Si atoms tip we have used in our simulations (Microscopic VdW) and to a macroscopic spherical tip with the experimental curvature radius of 40 Å. The covalent bonding interactions give a very significant contribution to the normal force and dominate the force gradient.

charge transfers observed during the scanning process (see [6] for details).

The comparison of the chemical bonding effects described above and the Van der Waals interaction (calculated using the standard Hamaker summation method [16]) indicates that covalent bonding interactions not only give a very significant contribution to the normal force even when compared with the macroscopic VdW interaction (which does not vary significantly from point to point across the surface and cannot produce atomic resolution), but dominates the force gradients, which drive the frequency changes used to create the experimental images (see Table 1).

3.2. Displacement curves

The dependence of the signal that is used to derive the image with respect to the distance between probe and sample is essential for the resolution of a scanning probe microscope.

Fig. 2 shows the total energy and normal force as a function of the tip–surface distance for different surfaces and the two saturated tips. We have considered the 10 Si atom tip on top of the corner hole and the faulted diagonal adatom on the 5 × 5 reconstruction, and the 4 Si atom tip on top of the unfaulted adatom on the 3 × 3 reconstruction. Those results are also compared with the interaction of the dangling bonds of two 4 Si atom tips.

All the curves show a striking similarity in the attractive part of the interaction, which further confirms that the tip–surface interaction obtained in our simulations are due essentially to the interaction of two silicon dangling bonds. On the other hand, there is an obvious difference in the position of the minima, both in the total energy and the normal force. The key to understand these differences is that when forces are present, the relative movement of tip apex and surface atoms is no longer the same as that of more distant parts of tip and sample. Our calculations show important relaxations even for a tip–

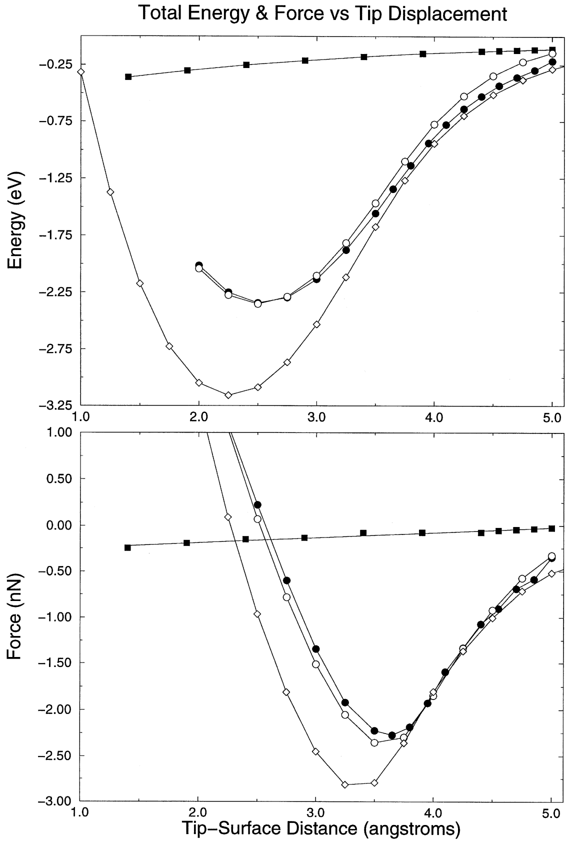

Fig. 2. Total energy (in eV) and normal force (in nN) as a function of the tip–surface distance for different surfaces and the two saturated tips. Black circles (squares) correspond to the 10 Si atom tip on top of the faulted diagonal adatom (corner hole) on the 5×5 reconstruction, and white circles to the 4 Si atom tip on top of the unfaulted adatom on the 3×3 reconstruction. Those results are compared with the interaction of two 4 Si atom tips (white diamonds). Notice the similarity of all the curves in the attractive regime. The differences in the position of the minima are related to relaxations of tip apex and surface adatoms, as explained in the text.

surface distance of 5 Å, where the actual apex–adatom (apex–apex) distance after atomic relaxation is allowed is 4.72 Å for the 5×5 reconstruction, 4.77 Å for the 3×3 and 4.92 Å for the two 4 Si atom tips, with this effect becoming increasingly important as tip and surface get closer. Differences among the curves thus reflect the different atomic relaxations due to the different bonding of the adatoms to the surface on the various systems considered. In all the cases the minimum in the total energy (and zero in the normal force) corresponds to the tip position where the apex–adatom distance is equal to 2.35 Å, the Si–Si nearest neighbour distance in bulk Si.

4. Discussion

The results presented above show that, at distances of 5 Å, there is a covalent chemical interaction between the dangling bonds of the adatoms in the surface and the apex atom in the tip that gives a contribution to the normal force comparable to the macroscopic VdW interaction and dominates the force gradients, providing a mechanism for atomic resolution imaging of reactive surfaces. The large differences in normal forces and force gradients among different atomic sites on the unit cell, with clear maxima on the adatoms, obtained in the simulations correlates with all the experimental images, taken at constant frequency shift, which show maxima in the tip–surface distance at the adatom positions.

Our results for the different tips suggest an explanation for the sudden switch of the tip to atomic resolution observed in the experiments of Giessibl [2,3] in terms of changes in the structure of the tip (picking up a Si atom from the surface, or losing a contaminant) which affect the electronic charge density distribution at the apex [6]. Similar effects have to be present on the experiments in Ref. [9] where only after an extensive scan with a W tip, they start observing an atomically resolved image.

The role of these dangling bond interactions is also supported by the fact that the onset of tunneling current and the rapid variation of frequency shift are taking place at a very similar tip–surface distance, when they are recorded simultaneously [7]. We note that the presence of localized dangling bond states in the apex of the tip has already been proposed to explain the enhancement of atomic resolution observed with the STM on silicon surfaces [17,18]. Further support comes from the recent experimental images in Ref. [8], where a dramatic improvement in resolution is observed after tip treatment.

Displacement curves explain the difficulty in achieving stable operation in the frequency shift mode due to the change of slope of the normal force (change of sign for the force gradients) taking place in a small distance range. A direct quantitative comparison of calculated force gradients and measured frequency shifts is still precluded due to the complicated dynamics of the cantilever. Our results for different surfaces show that realistic dynamical simulations of the tip movement, specially on the closer approach relevant to the damping experiments, where new phenomena like contrast between different adatoms is observed [9], really need a proper description of the response of the adatom, which can be parametrized from our calculations.

5. Conclusion

We have presented the first quantum mechanical simulations of the operation of the non-contact AFM. Our simulations show that, even at distances of 5 Å, there is a covalent chemical interaction between the dangling bonds of the adatoms in the surface and the apex atom in the tip which is comparable in magnitude to the macroscopic tip–surface VdW interaction. This interaction dominates the force gradients and provides a mechanism for atomic resolution imaging of reactive surfaces. Recent experimental evidence supports this contrast mechanism. Our results suggest that the sudden switch of the tip to atomic resolution observed in some of the experiments can be attributed to localized dangling bond states in the apex of the tip which are produced by structural changes which occur during the scanning process. Displacement curves provide a determination of the distance range for stable operation and show the relevance of a proper description of the relaxation of the tip apex and surface atoms to understand the experimental damping images.

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