Role of Covalent Tip-Surface Interactions in Noncontact Atomic Force Microscopy on Reactive Surfaces

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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 some parts of the experimental images is attributed to the onset of covalent bonding between a localized 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, and provides a mechanism for atomic resolution imaging on reactive surfaces. [S0031-9007(96)02218-1]

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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 noncontact attractive regime is a challenging experimental problem. Only recently have Giessibl [2] and Kitamura and Iwatsuki [3] shown atomic resolution in the noncontact (UHV) regime using a Si tip scanning a reactive surface, the reconstructed Si(111) 7×7 surface. These experiments use a novel frequency modulation detection scheme [4] that senses the force gradient, instead of the force itself.

A quick comparison of the AFM images in Refs. [2,3] with the STM images of the same surface shows that we are still far from an equivalent performance. Giessibl's experiment shows 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 [5] can be clearly seen. After this, the resolution deteriorates again, and no image is 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. Unfortunately, very little is known about the complex nature of the forces acting between tip and sample. Experiments probing the short-range metallic tip-surface adhesion find that concepts based on bulk adhesion are not generally applicable to describe the observed forces [6]. Accurate *ab initio* calculations are computationally demanding and only simple systems with a high degree of symmetry have been investigated [7]. The theoretical description of the noncontact regime is further complicated because of the need to accurately describe the interaction in a region where the crossover between chemical bonding and long-range Van der Waals (VdW) interactions should be taking place. Recent advances in massively parallel computing, coupled with improved algorithms for the implementation of total-energy pseudopotential calculations [8] and the new gradient approximations for the exchange correlation functional [9], now make it possible to use quantum mechanical simulations to improve our understanding of the mechanisms of image formation in noncontact AFM.

In particular, the work presented here addresses two questions motivated by the experiments: The nature of the interaction between tip and sample at the distance of closest approach (estimated to be 5 Å), and whether changes in the tip structure account for the variations in resolution observed [2].

We have addressed these questions by performing calculations for the 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 modeled using a supercell with inversion symmetry containing a 200 atom Si(111) slab, two tips (one on each side of the Si slab), and a vacuum region. The tips used in the experiment are etched out of single-crystalline Si. As the natural cleavage planes of Si are (111) planes, it is reasonable to consider that the very end of the tip is bounded by those planes. According to this model, we have

considered sharp tetrahedral tips with 4 (10) Si atoms stacked in two (three) Si(111) planes. 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 total dimension of the super-cell in the direction normal to the slab surface is 37.61 Å [equivalent to twelve double layers of the Si(111) struc-ture], providing a vacuum region of 6.86 Å between the larger tips in neighboring cells.

The operation of the microscope was simulated in a stepwise, quasistatic 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.

Optimized nonlocal pseudopotentials [10,11] were used to describe the Si ion cores. The pseudopotential was gen-erated to produce very similar p and d components and op-timized to make it rapidly convergent with the cutoff. The pseudopotentials were applied in the Kleinman-Bylander form [12], taking the p component as the local part and including only s nonlocal components, and using the real space projection technique [13]. 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 ener-gies and vibrational frequencies for the large system we are considering [14]. Finite temperature effects are not going to modify substantially our results since typical atomic fre-quencies are much larger than the tip oscillation frequency.

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 (see the inset of Fig. 1). 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.

Figure 1 shows the total energy [15] 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. All the tips show minima in the total energy at the position of the adatoms, but the minima
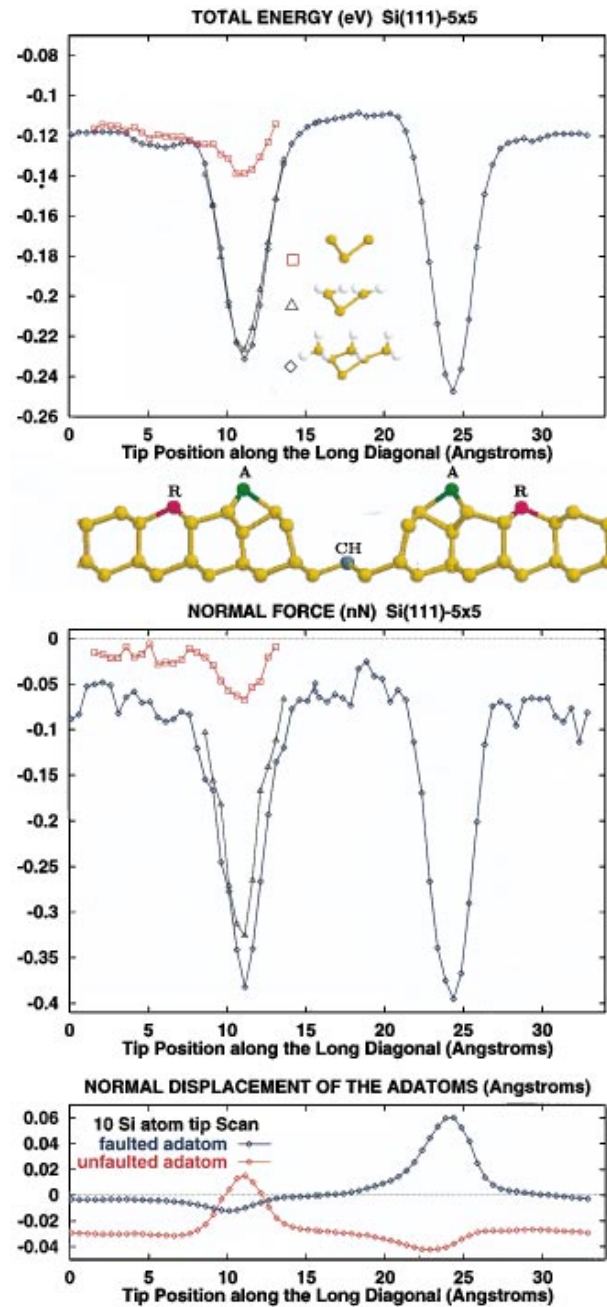

FIG. 1(color). Total energy (in eV) and normal force (in nN) for the two 4 Si atom tips scanning across one of the adatoms and a complete scan along the long diagonal of the 5×5 unit cell with the 10 Si atom tip at a constant height of 5 Å. Squares correspond to the 4 Si atom tip without a dangling bond, 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 inset shows a side view of the structure of the tips. A ball-and-stick representation of the atoms close to the lattice plane along the long diagonal is also included. The atoms with dangling bonds are 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.

are much deeper for the tips which have dangling bonds pointing towards the surface. Shallow minima can also be identified at the positions of the rest atoms. The differences found between the faulted and the unfaulted halves of the unit cell are related to the more effective charge transfer from the adatoms to the rest atoms in the unfaulted half. 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). The lowest binding energy and normal forces are found around the corner hole. 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.

We have carefully checked that these results are not significantly affected by the limited cutoff energy and k-point sampling used in our calculations. Test calculations at 11 Ry for the 5×5 reconstruction with the 10 Si atom tip show a very small reduction in the corrugation both in the energy (by 0.001 eV) and the normal force (by 0.012 nN), and further tests at 20 Ry on the 3×3 reconstructions confirm these findings with reductions of 0.016 eV and 0.026 nN. Tests on the 3×3 reconstruction show that the apparent corrugation increases with the accuracy of the k-point sampling and, with a slightly higher sampling density than used in the 5×5 calculations, gives results that are very similar to those presented above.

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 (shown at the bottom of Fig. 1 for the scan with the larger tip) and the charge transfers observed during the scanning process. The adatom closest to the tip moves upwards by as much as 0.06 Å and accumulates charge in its dangling bond, while the other adatom in the long diagonal moves downwards and charge is removed from its dangling bond. This transfer of charge towards the dangling bond of the adatom closest to the tip from the rest of the dangling bonds on the surface is illustrated in Fig. 2, where a plot of the charge density difference between the total system, when the tip is on top of one of the adatoms, and the isolated tip and surface is shown. Results for the scan along the off-diagonal adatoms show a similar pattern and will be discussed elsewhere [16]. All the scans show the extreme sensitivity of the normal force to the normal position of the adatoms. The lateral resolution, estimated from the half-width of the peaks in the force curve, is of the order of 3 Å.

It is interesting to compare the relative contribution of the chemical bonding effects we have described above and the Van der Waals interaction to the total normal force between the tip and a Si surface. We have employed the standard Hamaker summation method [17], which is based on an interatomic VdW pair potential of the form $w(r) = -C/r^6$, and where the interaction is assumed
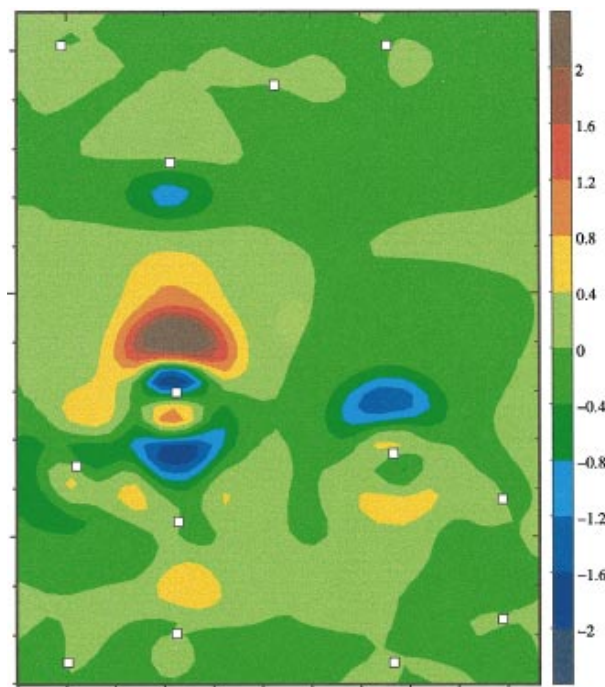

FIG. 2(color). Charge density difference between the self-consistent electron density of the interacting system and the superposition of the densities of the isolated tip and the clean surface. The plot corresponds to a plane perpendicular to the surface along the long diagonal (only part of the unfaulted half of the unit cell is shown). The tip is on top of the adatom on the long diagonal in the faulted half of the unit cell (the point of maximum bonding energy and normal force in Fig. 1). The squares indicate the position of the atoms in that plane both in the tip and in the Si surface. The contours are in units of 10^{-2} electrons/Å^3. Notice the transfer of charge to the adatom dangling bond from the backbond and the dangling bond in the rest atom.

to be nonretarded and additive. Summing (integrating) the different interatomic contributions one can obtain, for example, the interaction for an atom near a surface or a sphere near a surface [18]. Normal forces and force gradients have been calculated for the 4 Si atom tip used in our simulations and for a macroscopic spherical tip with the experimental curvature radius of 40 Å interacting with an ideal, continuous Si surface, assuming the normal distance between the top surface layer and the tip equal to the tip-adatom distance in our scan. It should be noticed that this model provides an upper bound for the VdW interaction with a 5×5 reconstructed surface. Table I compares the VdW results for a normal distance of 5 Å with those obtained in our *ab initio* simulation. The covalent bonding interactions 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. More importantly, the force gradients, which drive the frequency changes used to create the experimental images, are dominated by covalent bonding interactions.

The magnitude of the force gradients also accounts for the experimental observation that the feedback becomes

TABLE I. 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. The VdW values correspond to the 4 Si atom tips 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.

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

unstable at an estimated height above the surface of 5 Å. At this height, the values of $10-12$ N/m calculated for the force gradient are very close to the force constant of the piezolever used (17 N/m), and therefore jump to contact is very likely to happen.

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] in terms of changes in the structure of the tip which affect the electronic charge density distribution at the apex. If the tip moves closer to the surface, it can pick up a Si atom from the surface, or it can lose a contaminant previously attached to it. In this case, if a dangling bond directed towards the surface is formed, the contrast will be dramatically enhanced until that dangling bond is saturated again. These processes are more likely to happen in the experiments of Ref. [2] than in the ones of Ref. [3], where a much stiffer piezolever (force constant of 40 N/m) is used and so fluctuations in the tip-surface distance are expected to be smaller. In fact, no noticeable increase in the quality of the images was observed in this case during the scanning process. Finally, 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 [19].

In conclusion, we have presented the first quantum mechanical simulations of the operation of the noncontact 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. Our results suggest that the sudden switch of the tip to atomic resolution observed in the experiments of Giessibl [2] 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.

Note added.—Since the submission of this manuscript we have become aware of three experimental references [20–22] which give support to our conclusions.

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