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Tip–surface interactions in atomic force microscopy: reactive vs. metallic surfaces

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Abstract

We present ab initio simulations of AFM image formation in the non-contact regime for prototypical reactive semiconductor and metal surfaces: InP(1 1 0)-1 × 1 and Cu(0 0 1). For the reactive surface the effect of tip morphology of the tip apex was also studied. The nature of the tip apex alters the local tip reactivity and can lead to reversal of the apparent AFM surface corrugation. We find that for both semiconductor and metal surfaces the atomic resolution is primarily mediated by a strong chemical-type of interaction between the tip and the surface. This allows for a unified interpretation of the tip–surface interactions in the non-contact AFM microscopy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Non-contact AFM; Tip–surface interactions; Density functional calculations

Atomic force microscope (AFM) [1] has developed to one of the most powerful probes of atomic structure of both insulating and conducting surfaces. Of the different operation modes [2], only AFM operating in non-contact (attractive) regime in ultrahigh vacuum has demonstrated the ability to achieve true atomic resolution. Most of these experiments use the frequency-modulated AFM (FM AFM) [3], also subject of the present paper. Non-contact AFM has been used mainly to image the reactive surfaces: Si(1 1 1)-7 × 7 [3–5], Si(0 0 1)-2 × 1 [6], the polar III–V (1 1 0) surfaces: InP(1 1 0) [7,8], GaAs(1 1 0) and InAs(1 1 0) [2,9,10], ionic crystals [11], as well as defects on these surfaces [6–8].

Theory has provided very strong indication that on reactive surfaces the short-range chemical-type of tip–surface interaction significantly enhances the atomic resolution of the FM AFM [12–15]. Experiments have corroborated these conclusions [5,6]. Furthermore, the fact that the atomic resolution is primarily mediated by a dangling bond type of interaction between the atoms on a sample surface and a tip is in accordance with the ability to resolve a number of different atoms (dangling bonds) on the Si(1 1 1)-7 × 7 surface [16,17], whereas on polar surfaces, such as InP(1 1 0) and GaAs(1 1 0) only the anion sublattice could be resolved under usual experimental conditions [7,8]. These are manifestations of the tip having different "local reactivity" with the surface. In addition, the theoretical studies [15,18] using classical perturbation theory [19,20] for the tip–surface interaction treated within density functional theory (DFT) [21] to compute the frequency shifts have been shown to provide a

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sound basis for understanding the FM AFM experiments.

The first non-contact AFM images of metallic surfaces showing true atomic resolution started to appear only very recently [2]. Loppacher et al. [22] and Orisaka et al. [23] presented true atomic resolution for Cu(1 1 1), Cu(0 0 1) and Ag(1 1 1), respectively. While the role of chemical tip–surface interaction has long been demonstrated theoretically [12,13] and experimentally [5,16], the existence of such a strong chemical-type of (covalent) tip–surface interaction is much less obvious for a metal surface. To the best of our knowledge, no ab initio theoretical study of this phenomenon exists for a metallic surface. It is the purpose of this paper to conduct such a study. We first present results for a reactive surface, InP(1 1 0), and then compare them with results of a very recent study of the Cu(0 0 1) surface.

Our model for the tip–surface interaction in the near contact short-range regime is based on DFT [21] in its plane-wave pseudopotential formulation. Technical details for the InP(1 1 0) surface are described in [18] and for the metallic Cu(0 0 1) surface will be published elsewhere [24]. These simulations include only the short-range interactions. We make no attempt to include also the long-range interactions, such as van der Walls. Those are, unlike the chemical short-range interactions, strongly dependent on the tip size and shape. They can be comparatively easily included once the tip size and shape are known or a model for them adopted [13,20]. The surfaces are described by a slab model. Both experiments [7,8,22] used Si tips which we model by small Si tips saturated at the tip base by H atoms [15]. The main characteristics of the pure Si tip is the presence of one singly occupied dangling bond sticking out of the tip apex. This dangling bond is instrumental in the atomic resolution of the FM AFM on a reactive surface and as shown below also on a metallic surface. The structural models used in our study are shown in Fig. 1. The main difference between the two models is that: (1) to emulate the bulk termination of the slab we saturate the dangling bonds on one side of the InP slab by hydrogen; (2) a smaller, 4-Si-atom tip is used on the Cu surface. The smaller tip is used to make the much more computationally involved metallic calculations more feasible by allowing to keep the lateral cell size smaller. The rational for using such a small tip size is

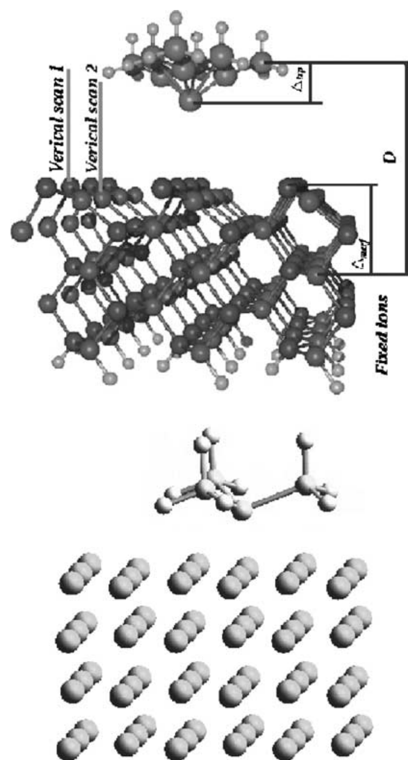

Fig. 1. Structural models used for: upper panel InP(1 1 0) surface, bottom panel Cu(0 0 1) surface.

the finding that the short-range interactions exhibit only very small dependence on the size of the tip [13]. The apex, and for a 10-Si-atom tip also its three nearest neighbor Si atoms, are allowed to relax. We have performed a number of vertical scans by moving stepwise the tip positioned over a chosen site in the surface unit cell allowing for a full relaxation of the tip as well as non-fixed surface atoms. Significant relaxation of both the tip as well as surface atoms underneath the tip is observed. The sum of the forces exerted on the fixed atoms of the tip is taken to be the total tip–surface force. On the InP surface we have studied also the effect of tip morphology by modifying the tip apex. We have considered three different tips: Si tip with a Si apex (Si/Si tip), Si tip with an In apex (In/Si tip), and a Si tip with a P apex (P/Si tip). Such modifications of the tip apex may easily result from accidental contact of the tip with the surface. These tips are shown in Fig. 2. The Si/Si tip is characterized by a singly occupied dangling bond, the In/Si tip by an empty

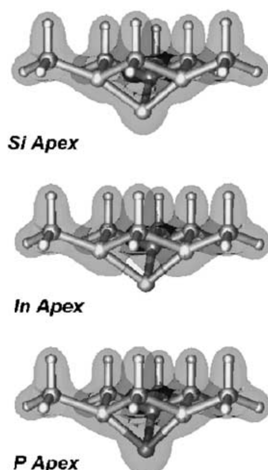

Fig. 2. Tips used in the simulation with superimposed isosurface of valence electronic charge density. Upper panel: Si/Si tip; middle panel: In/Si tip; bottom panel: P/Si tip.

dangling bond and the P/Si tip by a doubly occupied dangling bond.

The prominent feature of the InP(1 1 0) surface is its stabilization by buckling [15,25] which causes the P (In) surface atoms relax upwards (downwards) and the dangling bond states on P (In) atoms to populate (depopulate). As a result, most of the surface reactive charge is floating on the P atoms. The results for the normal tip–surface force and frequency shifts over the In and P sites for the three different tips are shown in Fig. 3. The frequency shifts were computed using classical perturbation theory [19,20] with $V_p(q)$, the tip–surface interaction computed in the DFT theory, treated as perturbation. As shown in Fig. 4, the tip–surface interaction in the near contact region is significantly enhanced by short-range covalent bond formed between the tip and the surface dangling bonds. As expected, the Si apex interacts more strongly with the P site than with the In site. Interaction of the In/Si tip with the surface is reduced by a factor of ≈2, compared to the Si/Si tip. Nevertheless, qualitatively both apexes yield similar results. Situation changes dramatically in the case of a P apex. Due to the doubly occupied P dangling bond state there is very little interaction with the surface P site up to distances of ≈3 Å. At that distance a strong rebonding at the tip apex starts. One of the Si–P bonds in the tip is broken and two more tip–surface bonds are formed (one P–P and one Si–In bond). Hence, the strong tip–surface interaction is a consequence of formation of a double bond between the tip atoms and the surface. These bonds exert significant lateral forces on the tip. Better insights into the complex nature of the tip–surface interaction can be obtained from computer graphics.[1] The tip–surface bonding translates into the behavior of the frequency shifts. The experimental value $\Delta\omega = -6$ Hz [7] yields for the Si/Si tip a computed AFM corrugation of ≈0.3 Å [15], in excellent agreement with the experimental value [7]. This is an indication that extremely sharp tips must have been used in the experiments as no long-range component is included in our model. In the case of an In apex, our model predicts that a measurable In–P corrugation should start appearing for $\Delta\omega \leq -4$ Hz. The P apex represents a qualitatively different scenario where the In sublattice may have a higher apparent AFM height. This result gives a very clear indication how the ‘‘local reactivity’’ associated with tip apex morphology may affect the formation of the AFM image.

It is interesting to compare the nature of a tip–surface interaction for a reactive semiconductor surface with results for a metal surface. Such a study is necessary in order to interpret the recent experiments performed for metallic surfaces [22,23]. The covalent bond formed between the dangling bonds on the tip apex and dangling bonds on a semiconductor surface is much less likely to form on a metallic surface with significantly less localized reactive charge. For that reason other types of tip–surface interaction might be envisaged. We have performed a study for a Cu(0 0 1) surface [22]. Preliminary results for vertical scans over on-top and hollow sites are shown in Fig. 5. A more complete account of these results will be published elsewhere [24]. From the energy curve, we see that at variance with reactive surfaces where the tip was primarily reacting with the dangling bonds on the surface atoms, on the metal surface the minimum of the energy is over the hollow site. Nevertheless, larger forces result from the on-top position. From these curves, we infer that the FM AFM will image the atomic positions. The most striking result from our metal simulation is that the interaction of the Si tip with the Cu(0 0 1) surface is almost indistinguishable from the interaction with the reactive semiconductor

[1] A computer graphics animation of the simulation can be downloaded from http://www.ccms.elf.stuba.sk/index.html.

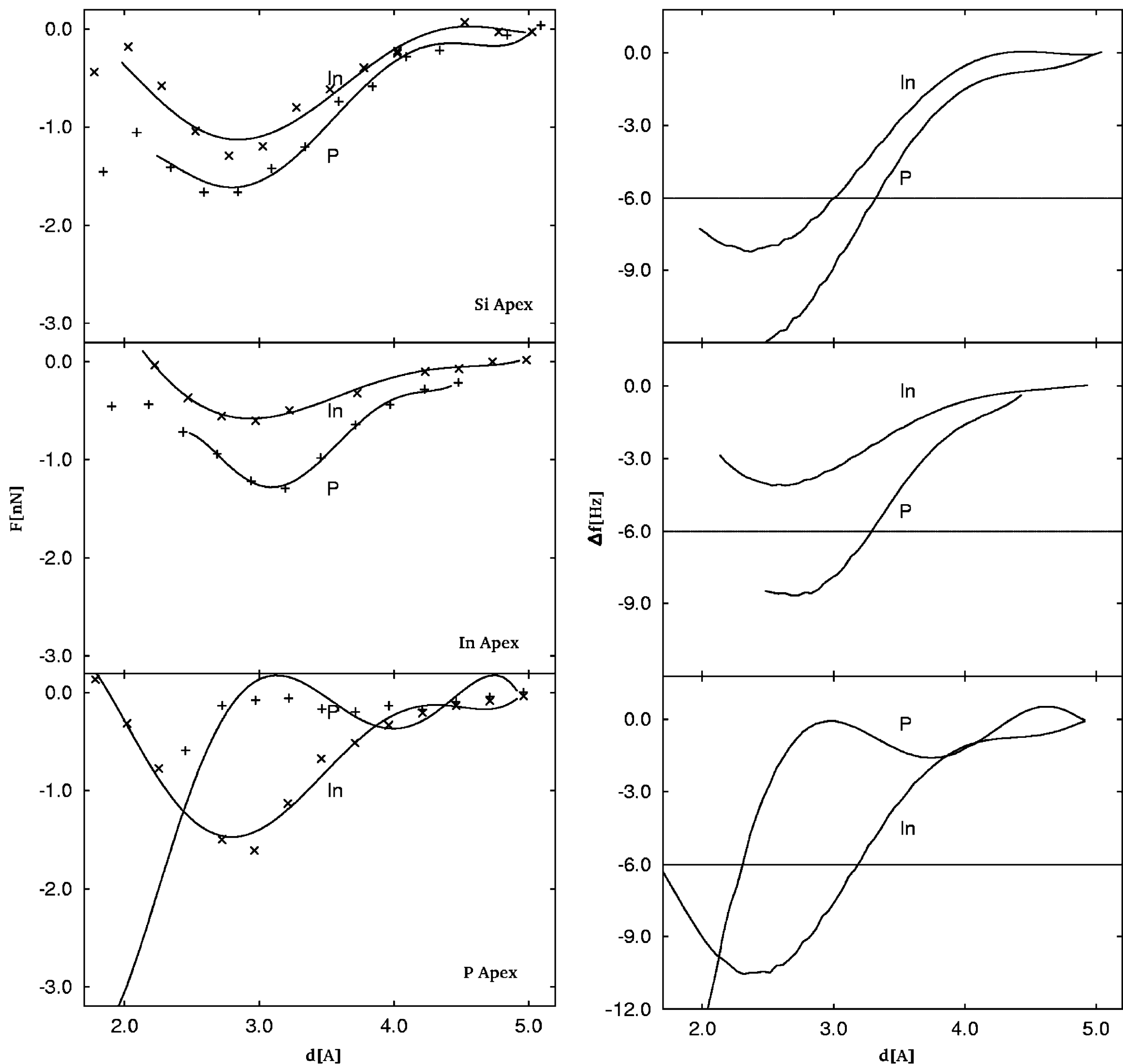

Fig. 3. Normal tip–surface forces (left panel) and frequency shifts (right panel) in vertical scans performed with the Si/Si tip (upper panel), In/Si tip (middle panel), and P/Si tip (bottom panel) over In and P sites. Experimental parameters were taken from [7]. The horizontal line at −6 Hz corresponds to the experimental $\Delta\omega$.

surface (cf. Fig. 4). Hence, despite the more delocalized reactive charge, a very well-localized bond between the tip and the metal surface is formed. At small tip–surface distances multiple bonds are formed. These bonds induce weak lateral forces on the tip. One consequence of this bonding situation is that in the on-top position there is a large surface response with the surface Cu atom relatively strongly bonded to the tip and following its motion. We have found that a dipole is formed when the tip approaches the surface. However, the change of the dipole as a function of the tip–surface distance is negligible. A better insight may be gained from a computer graphics animation.[1]

In conclusion, we have presented a simulation and comparison of tip–surface interaction on a reactive semiconductor surface and a metal surface. The comparison was based on a DFT simulation for InP(1 1 0) and Cu(0 0 1) surface. For the InP(1 1 0) surface the

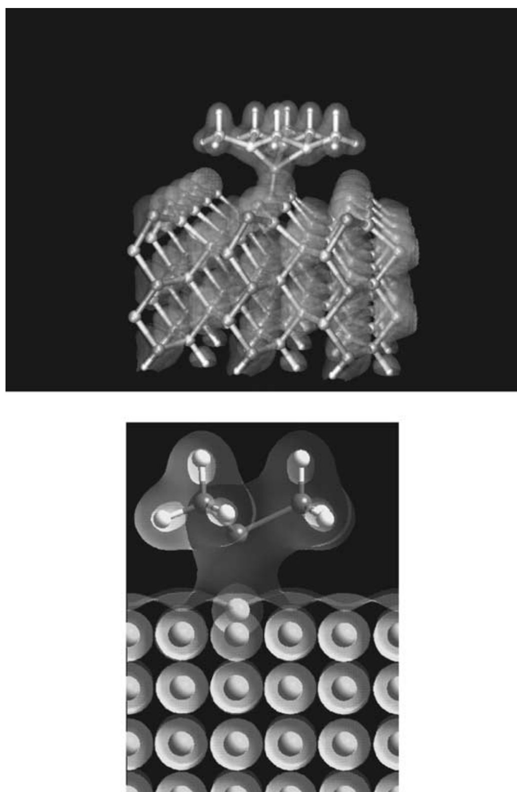

Fig. 4. Chemical bond formed between the tip and the surface. Upper panel: InP(1 1 0) surface and P/Si tip; bottom panel: Cu(0 0 1) surface and Si tip.

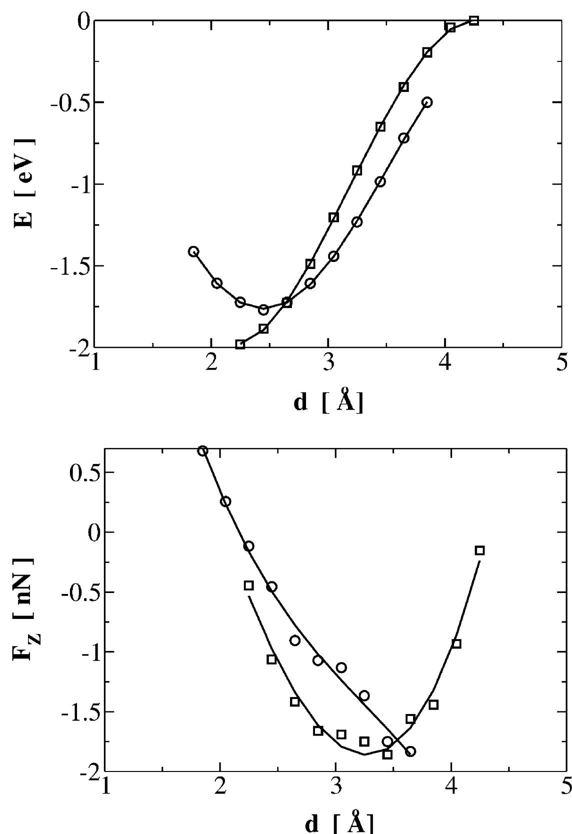

Fig. 5. Vertical scans over the on-top (○) and hollow site (□) for the Cu(0 0 1) surface. Upper panel: total energies; bottom panel: normal tip–surface forces.

effect of tip morphology was also studied. We find that the local tip reactivity with the surface is significantly altered by the tip morphology, specifically by the tip apex. The results obtained with the Si tip with Si apex showed very good agreement for surface corrugation with the experimental results. The simulation also suggests that the experimental image should exhibit only protrusions associated with the anion sublattice, on the other hand, the P apex causes reversal of the apparent AFM corrugation with respect to the Si and In tips as well as with respect to the geometric corrugation. A simulated AFM image with the P/Si tip exhibits protrusions associated with the cation (In) sublattice. The comparison of the tip–surface interaction between the semiconductor and metal surface exhibits that, despite the much more delocalized nature of the valence electronic charge on the metal surface, in both cases the tip forms a very strong and localized bond to the surface. Hence, the mechanism of atomic resolution in both cases can be traced back to strongly localized chemical bonds between the tip and the surface. The complexity of the tip–surface interaction on both types of surfaces suggests that understanding and interpretation of FM AFM images is of similar complexity to understanding the STM images and a theoretical study of image formation can provide valuable insights.

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