Atomic-Scale Sharpening of Silicon Tips in Noncontact Atomic Force Microscopy

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The atomic-scale stability of clean silicon tips used in noncontact atomic force microscopy (NC-AFM) is simulated by *ab initio* calculations based on density functional theory. The tip structures are modeled by silicon clusters with [111] and [001] termination. For the often assumed Si(111)-type tip we observe the sharpening of the initially blunt tip via short-range chemical forces during the first approach and retraction cycle. The structural changes corresponding to this intrinsic process are irreversible and lead to stable NC-AFM imaging conditions. In opposition to the picture used in literature, the Si(001)-type tip does not exhibit the so-called ''two-dangling bond'' feature as a bulklike termination suggests.

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The *atomic force microscope* (AFM) [1] has been developed as a tool for real-space imaging of conductor, semiconductor, and insulator surfaces. However, true atomic resolution on these surfaces is only obtained by *noncontact atomic force microscopy* (NC-AFM) [2,3]. Later on, this technique was extended to *dynamic force spectroscopy* (DFS) enabling the precise detection of the tip-sample interaction forces at specific lattice sites [4–6], or to measure the switching of single molecules [7].

Both techniques rely on the measurement of the forces acting between an atomically sharp tip and a sample surface. From the experimental point of view, a stable operating regime in NC-AFM which provides reproducible atomic-scale images is quite often difficult to obtain. The basic reason resides in the fact that the tip-sample interaction does not vary monotonically with the tip-surface separation distance. Furthermore, it is important to note that the geometrical and chemical structure of the AFM tip before and during an NC-AFM experiment are *not* known. This implies that its apex structure might change during the imaging process due to the interaction between tip and sample. A possible scenario is that some material of the sample might be picked up by the tip [6]. A different tip morphology might result in a quite different image contrast [see, for instance, Fig. 3 in Ref. [8] and the calculations in Ref. [9,10]].

Besides this, it was recently argued that *different* crystallographic orientations of a silicon tip might lead to a significant change in the structure of the NC-AFM images. Giessibl *et al.* [11], for example, reported the experimental observation of a subatomic (orbital) structure of the adatoms on the Si(111)-(7 × 7) surface. Their analysis was based on the assumption that a silicon tip with [001] termination exhibits two-dangling bonds which sense the dangling bonds of the adatoms. This result was questioned by Hug *et al.* [12], but supported by the simulations of Huang *et al.* [13] even if the tip atoms were not allowed to relax in their first-principles calculations.

Thus, to establish a detailed understanding of the NC-AFM imaging process, an insight into the role of the geometry and structural changes of the AFM tip during the NC-AFM imaging process is required. To some extent, such *ab initio* studies have been performed in the past for semiconductor [10,14,15] and insulator [16,17] surfaces. However, these studies were confined to a *particular* choice of the AFM tip with a specific apex geometry and chemical nature of the front atoms. Moreover, the details of the tip's behavior might be particular to the *specific* surface under investigation.

In this Letter we report about our first-principles calculations carried out in order to investigate the possible structural changes of clean silicon tips during the NC-AFM imaging process and their implications on the contrast of the recorded images. Instead of analyzing the interaction of an AFM tip with a *certain* surface, we have investigated the structural changes of the tip apex itself [18]. To do that we approach a very stiff tip to the tip under consideration and analyze the induced *tip-tip* interactions. The basic motivation of this choice is that we would like to unveil those features which describe an *intrinsic* behavior of clean silicon tips.

For a Si(111)-type tip the theoretical force curves exhibit a hysteretic behavior only during the first approach and retraction. The hysteresis is due to an *irreversible* change of the atomic tip structure leading to the sharpening of the initially blunt tip. This intrinsic process of tip's sharpening corresponds to an additional energy dissipation in NC-AFM to that due to *reversible* structural changes of the tip-sample system. A Si(001)-type tip shows negligible hysteresis during approach and retraction. The astonishing feature of this tip is the absence of two-dangling bonds on its apex atom as it is suggested by a bulklike termination.

The later result is in opposition to the model of a ''two-dangling bond'' tip assumed in Refs. [11,12]. The obvious reason for this is that they used an empirical Stillinger-Weber potential [19]—originally developed to describe

bulk properties. It also contradicts a similar tip model used in Ref. [13].

Tip model and computational method.—First-principles total energy calculations of the isolated and interacting silicon tips have been performed within the framework of density functional theory [20] in the local density approximation [21]. To solve self-consistently the Kohn-Sham equations we employed the pseudopotential method [22] as implemented in the ESPRESSO package [23]. For the silicon atoms the full ionic potential was replaced by a smooth norm-conserving pseudopotential using the scheme proposed by von Barth and Car [24] while for hydrogen atoms we used the bare Coulomb potential. All our *ab initio* simulations have been done using orthorhombic supercells of $18 \times 18 \times 20$ $(\text{Å})^3$. To ensure a good description of the electronic charge density in these supercells, we employed a plane wave basis set generated by a cutoff energy E_{cut} of 45.0 Ry. The Brillouin zone integrations for all supercell calculations have been done using the Gamma point. In order to perform accurate structural relaxations of the considered silicon tips, the calculated interaction forces have an accuracy better than 5×10^{-5} Ry/(atomic units).

The tips used in our first-principles simulations are clusters of silicon atoms of different sizes cut along [111] and [001] directions of the bulk silicon. The results presented here were obtained with a $Si_{13}H_{15}$ cluster [Si(111)-type tip; Fig. 1(a)] and a Si_7H_{12} cluster [Si(001)-type tip; Fig. 1(b)]. To examine the structural changes of these silicon tips, both types of tips were approached towards a $Si_{10}H_{15}$ cluster with [111] termination [Fig. 1(e)]. The geometrical and electronic structure of this type of tip was already discussed in literature [see, for example, Refs. [25,26] and references therein]. It was shown that such type of tip is stiff and sustains large forces during the scanning of a diamond surface [26].

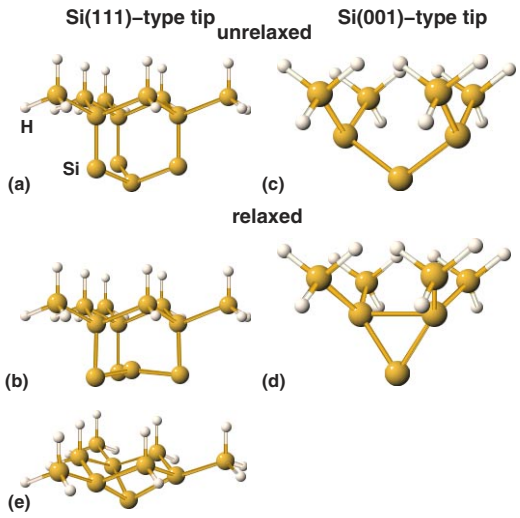

FIG. 1 (color online). Ball-and-stick model of the atomic structure of the isolated silicon tips with [111] and [001] termination: (a) and (b) show the unrelaxed and relaxed structure of a $Si_{13}H_{15}$ cluster [Si(111)-type tip]. (c) and (d) represent the unrelaxed and relaxed structure of a Si_7H_{12} cluster [Si(001)-type tip]. (e) Both types of tips were approached to the relaxed structure of a $Si_{10}H_{15}$ cluster with Si(111) termination.

The change of the geometrical structure of all tips due to their reciprocal interaction was considered by fixing the silicon atoms of their base (6 atoms for the two [111] terminated and 4 atoms for the [001] terminated tips) while all other silicon atoms were allowed to relax. The hydrogen atoms have been used only to saturate the base atoms of the silicon tips. Consequently, they were kept fixed during atomic relaxations.

Isolated silicon tips.—The unrelaxed geometrical structure of a Si(111)-type tip is illustrated in Fig. 1(a). In this unrelaxed configuration, this tip exhibits one dangling bond due to a bulklike threefold coordination of its apex atom as shown in the electron density plot in Fig. 2(a). However, the relaxed structure presented in Fig. 1(b) reveals a strong relaxation of the apex atom into the tip structure. The total energy difference between the relaxed and unrelaxed configuration of this tip is about -1.04 eV. In consequence, this tip is by its nature *blunt* and the corresponding electron density of its apex structure is more diffuse than that of the unrelaxed tip [Fig. 2(a)]. This result demonstrates the importance of the relaxation of this type of tip. This effect, for example, was not observed in of Ref. [13] because the tip was not allowed to relax.

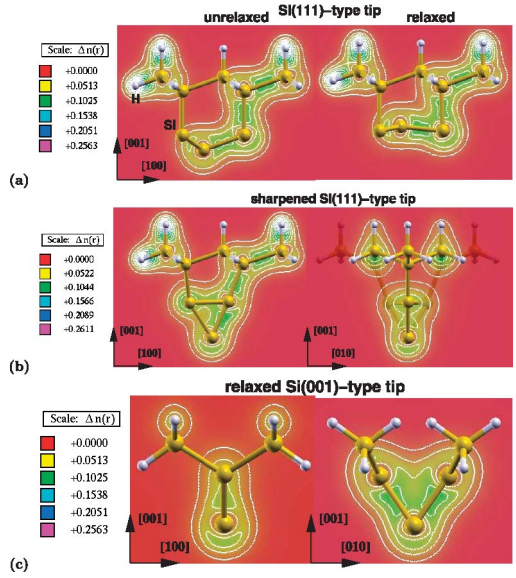

FIG. 2 (color). (a) Charge density plots of the unrelaxed (left) and relaxed (right) structure of the $Si_{13}H_{15}$ tip. The relaxed structure is blunt and the charge density of the four front atoms has a diffusive character over these atoms. (b) Charge density plots of the $Si_{13}H_{15}$ tip sharpened via short-range chemical forces corresponding to (010) and (100) crystallographic planes (left and right, respectively). (c) Charge density plots of the relaxed structure of the Si_7H_{12} tip [see Fig. 1(d)]. The calculated charge density has an axial symmetry without any "two-dangling bond" feature at its apex atom. All charge density plots have been done using the XCRYSDEN program [31].

The atomic unrelaxed structure of a silicon tip with [001] termination is shown in Fig. 1(c). A similar but smaller tip was assumed by Huang *et al.* [13] in order to establish if the atomic orbitals can be resolved by NC-AFM as suggested by Giessibl *et al.* [11]. The relaxed structure of this tip is presented in Fig. 1(d). The basic difference between the unrelaxed and relaxed structures consists in the formation of a chemical bond between two silicon atoms underneath the front atom. This is due to the fact that both silicon atoms had already one dangling bond.

More interesting is the electronic structure of this tip displayed in Fig. 2(c) in terms of electron charge density. The most striking feature is the *absence* of the two-dangling bonds on its apex atom. Instead, the electron density exhibits an axial symmetry and resembles the shape of a pear in the (010) plane. If the two electrons were confined in two-dangling bonds as a bulklike termination suggests, the Coulomb repulsion would increase the total energy of the system and therefore these electrons become delocalized over the three front atoms of the silicon cluster. This qualitative argument is also valid for an *unrelaxed* Si(001)-type tip whose electronic charge density looks very similar to the relaxed one. Therefore it does *not* exhibit a "two-dangling bond" feature as schematically depicted in Refs. [11,13].

Tip-tip interactions.—In Fig. 3(a) we present the force curves calculated during the first and second approach/retraction cycle of the Si(111)-type tip on the $Si_{10}H_{15}$ cluster. The important feature revealed by these theoretical force curves is the presence of a large hysteresis when the tips are approached and retracted for the first time, while this hysteretic behavior is *absent* at the second approach and retraction. This hysteresis is caused by a jump of the system into a different energy minimum.

As shown in Fig. 4(a) at atomic level this remarkable feature is due to the *sharpening* of the Si(111)-type tip. This process takes place when the tips are 3.8 Å apart from the smaller cluster and is related to the jump of one front atom of the apex atom of the Si(111)-type tip (top) towards the apex atom of the smaller one (bottom). This jump of one silicon atom leads to the formation of a tetragonally coordinated cage of silicon atoms which is, from a structural point of view, much more stable than the initial configuration. More specifically, the total energy difference of the isolated sharpened tip compared to the blunt one is about −0.86 eV. In addition, when this tetragonal unit of the Si(111)-type tip is formed, the corresponding sudden shrinkage of the distance between the tips results in a strong repulsive interaction. The charge density plots corresponding to two different crystallographic planes are shown in Fig. 2(b).

It is important to note that for such a tip the hysteresis is present only during the first approach and retraction path. During this cycle it underlies on an *irreversible* structural change from a blunt to a sharp tip. This effect is different from the model assumed to explain energy dissipation in NC-AFM [see, for example, Refs. [27–29]]. In such a case, the hysteresis is associated with *reversible* structural changes of the tip-surface system which have to appear for every approach and retraction curve. However, as shown by our *ab initio* simulations, the use of a blunt (soft) silicon tip leads to an additional contribution of the dissipated energy, only in the initial stage of the imaging process.

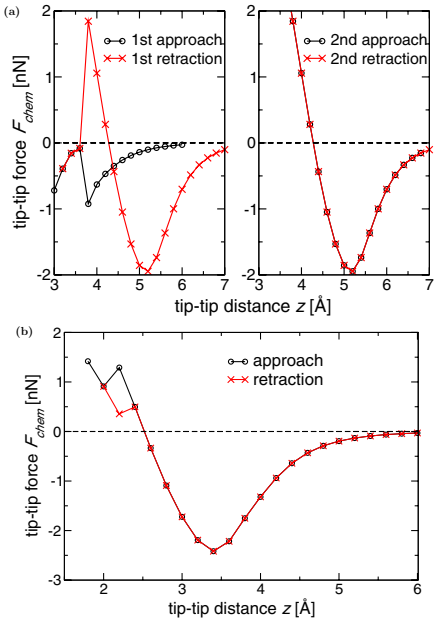

FIG. 3 (color online). The normal component of the short-range tip-tip chemical force F_{chem} due to the interaction between silicon tips with [111] and [001] termination. The step used during the approach and retraction paths was set to 0.2 Å. (a) Force curves of the first and second approach/retraction cycle of the Si(111)-type tip [see Fig. 1(a)] towards the smaller Si(111)-type tip [see Fig. 1(e)]. There is a significant hysteresis for the first cycle. Because of the short-range chemical interactions the atomic structure of the tip changes after the first scan and the tip is more stable. No hysteresis is observed in the second cycle. (b) The Si(001)-type tip is rather stiff and does not change significantly during the approach and retraction paths. A very small hysteresis can be observed in the repulsive regime due to breaking and formation of a chemical bond during approach and retraction [see the dashed line in Fig. 4(b)].

This structural "sharpening" is not only observed for this specific tip-tip configuration, but it was also obtained during the interaction of the Si(111)-type tip with the Si(001)-type one [30]. Additionally, we considered different tip sizes and possible spin polarization effects and we obtained always the same sharpening effect. Therefore, we conclude that the observed feature is a general effect for Si(111)-type tips. Several experimentalists report that atomic resolution in noncontact atomic force microscopy is typically obtained after a soft "crash" of the tip into the surface. The described sharpening effect serves as a plausible explanation for this experimental observation.

On the contrary, we do not observe a similar behavior for the Si(001)-type tip. The theoretical force curves corresponding to the interaction of the Si(001)-type tip with the $Si_{10}H_{15}$ cluster are plotted in Fig. 3(b). This tip exhibits

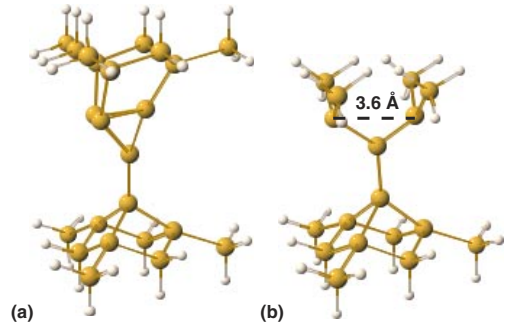

FIG. 4 (color online). Ball-and-stick model of the atomic tip structures during the interaction of silicon tips with [111] and [001] termination. (a) During the first scan, on the retraction path at a distance of 3.8 Å the initially blunt Si(111)-type tip (upper tip) becomes sharp due to the jump of one front atom towards the other bottom tip. (b) The small hysteresis due to interaction between Si(001)-type tip and the smaller cluster is associated with the breaking and formation of a chemical bond of two silicon atoms during the approach and retraction path. The broken chemical bond is indicated as a dashed line. The distance of the two silicon atoms increases from 2.6 Å to 3.6 Å during the bond rupture.

almost no hysteric behavior for all approach/retraction cycles. There is only a small difference between the approach and retraction paths corresponding to a tip-tip distance of 2.2 Å. At this position the bond between the silicon atoms underneath the front atom breaks or formates as illustrated in Fig. 4(b) by a dashed line.

In conclusion, we have investigated by means of *ab initio* pseudopotential calculations the atomic-scale dynamics of Si(111)- and Si(001)-type silicon tips. For a Si(111)-type tip our first-principles simulations revealed a mechanism for the sharpening of an initially blunt tip via short-range chemical forces. This process is accompanied by an irreversible structural change of this type of tip. After this process has taken place, a stable NC-AFM imaging becomes possible. For a Si(001)-type tip our calculations predict the absence of two-dangling bonds as one might expect by assuming a bulklike termination. However, it was shown by our simulations that the geometry of such a tip does not change significantly during vertical displacements and it should provide stable imaging in NC-AFM.

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