

Probing the Si(001) surface with a Si tip: An *ab initio* study

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Topographic noncontact atomic force microscopy (NC-AFM) images of the $p(2\times 1)$ and $c(4\times 2)$ reconstructions of the Si(001) surface are simulated for the cases of weak and strong tip-surface interactions and various temperatures using *ab initio* density functional theory. In the simulations the surface is imaged by a sharp silicon tip with a single dangling bond at its apex. At a very close approach to the surface, the tip flips a surface dimer when positioned close to its lower atom. The energy barriers for an individual flipped surface dimer to regain its initial configuration are calculated to be ~ 0.1 eV, implying that the surface should be able to “heal” itself at all but extremely low temperatures during one oscillation cycle of the cantilever. Thus, at small enough temperatures, $T \leq 70$ K, and large frequency shifts, the imaging process is dominated by tip induced dimer flip events resulting in a permanent deformation of the surface and an apparent $p(2\times 1)$ symmetric phase to be observed. No dissipation is expected as the tip oscillations are conservative at these conditions. At intermediate temperatures, $70 \text{ K} \leq T \leq 200 \text{ K}$, the flipped dimers are able to return to the ground state during each tip oscillation, resulting in continuous healing of the surface and thus large dissipation is expected. At $T \geq 200 \text{ K}$ dimers flip back and forth easily resulting in an apparent symmetric $p(2\times 1)$ phase and noticeable dissipation. At small frequency shifts the dimers do not flip, still the upper dimer atoms are imaged as bright so that surface reconstruction can easily be determined. The possibility of manipulating the orientation of dimers at low temperatures and large frequency shifts by means of preprogrammed scan directions, is also discussed.

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I. INTRODUCTION

The clean Si(001) surface has been a highly active area of research for many years with numerous publications addressing its physical properties, chemical reactivity, and its ground state configuration. When silicon is cleaved in the (001) direction the surface atoms are each left with two dangling bonds. Adjacent surface atoms then link up to form dimers to saturate one of the two dangling bonds, lowering the surface energy and creating a distinctive surface structure of parallel dimer rows separated by trenches. This surface structure was identified almost half a century ago in LEED experiments.¹ More recently, following the advent of scanning probe microscopy, the structure of the surface was resolved atomistically, with the parallel dimer row structure successfully confirmed both by scanning tunnelling microscopy (STM) (Refs. 2–6) and atomic force microscopy (AFM).^{7,8} Most recently, it has also been confirmed by the high-energy positron diffraction experiments.⁹

One of the most exciting features of the Si(001) surface is that the ground state configuration of the surface dimers is not symmetrical (see, for example, Refs. 10 and 11). It appears that a small amount of energy is gained if dimers buckle, i.e., adopt an asymmetric configuration at equilibrium. Depending on the relative orientation of the buckling that adjacent dimers adopt, various surface reconstructions become possible: (i) $p(2\times 1)$ in which all dimers in each row are buckled in the same way; (ii) $p(2\times 2)$ in which neighboring dimers in each row are buckled in the opposite directions, but every row is periodically repeated so that neighboring rows are buckled in-phase; and, finally (iii) $c(4\times 2)$ in which dimers buckling alternates both along and perpendicular to the row direction. Until recently, it has still been

unclear, both from the theoretical and experimental points of view, which of the three mentioned reconstructions correspond to the true ground state of the surface.

STM and AFM (Ref. 12) studies have been conducted at various temperatures in order to elucidate the actual orientation of dimers on this surface. STM images taken at room temperature yield a symmetric dimer structure that is attributed to a rapid flip-flop motion of the buckled dimers.^{4,10,13} Indeed, the energy barrier necessary for a dimer to flip has been estimated from theoretical calculations and found to be of the order of 0.1–0.3 eV.^{14–16} At room temperature this barrier is easily overcome and the dimers can rapidly reverse their buckling orientation, so that on average the dimers appear in the symmetric $p(2\times 1)$ structure.

Indeed, it follows from the LEED data^{17,18} that the surface undergoes an order-disorder phase transition at around 200 K from the low-temperature ordered to a high temperature disordered structure. The situation is analogous to the Ising lattice of spins, and, indeed, the analogy has been exploited in a number of theoretical papers^{19,20} where attempts have been made to devise a model Ising-type-Hamiltonian that describes the dimers orientations as “spins” (i.e., buckled in one or another direction). Normally, the parameters of the model Hamiltonians are drawn from *ab initio* calculated energies of periodic cells with various dimer orientations. These studies suggest that at temperatures of around and above 200 K the dimers can be considered to be oriented almost at random with equal populations of the two possible buckled orientations.

At intermediate and small temperatures the buckled $c(4\times 2)$ configuration is predominantly seen^{10,5,21} implying that this is the most energetically favorable dimer arrangement, i.e., the ground state of the Si(001) surface. However, this

conclusion has been recently compromised by some STM (Refs. 6, 4, 22, and 23) and LEED (Ref. 24) studies that suggested that there might be a phase transition at very low temperatures (below 40 K) at which dimers may become symmetric again. Several possible explanations were given to this effect. In Refs. 5, 23, and 25 it was argued that the dimers configuration may have been caused by the surface charging during the current flow in STM experiments. In Refs. 26 and 27 the appearance of the symmetric dimers at low temperatures during STM experiments was attributed to the p -type character of the substrate and defect density on the surface that may have stabilized the structure. They have also found that the major contribution to the STM images of symmetric dimer rows comes from the back-bond electronic states associated with the Si atoms that are directly underneath the Si dimers.

NC-AFM experiments are normally conducted using a small applied bias purely to compensate for the contact potential and so are “cleaner” in this respect than STM. Atomically resolved NC-AFM images of the Si(001) surface were obtained in Refs. 7 and 8 using the constant excitation mode at 5 K. These studies confirmed the existence of buckled dimers and it was concluded that the upper dimer atoms were imaged as bright spots. A distinctive zig-zag pattern was identified which was in antiphase across the majority of adjacent rows; this is characteristic of a $c(4 \times 2)$ reconstruction. There were also some $p(2 \times 2)$ regions observed in which the zig-zag pattern is periodically repeated across neighboring rows.

The question as to which of the surface reconstructions is the ground state of this surface has also been debated theoretically. *Ab initio* quantum chemistry cluster calculations performed at various levels of accounting for the correlation effects²⁸ indicate symmetrical dimers as the ground state of the system, whereas the density function theory (DFT) calculations within the same cluster models give the surface energy for buckled dimers to be lower.²⁸ *Ab initio* DFT calculations performed for a slab model predict a clear energy gain of ~ 0.3 eV per dimer when the surface dimers go from a symmetric to a buckled structure,^{10,29,30,19} i.e., they favor buckled dimers. More precise quantum Monte Carlo (QMC) calculations³¹ performed on relatively large cluster models of the surface found the $c(4 \times 2)$ configuration to have a lower energy than the structure with symmetric dimers, whereas another QMC study³² was inconclusive. Note, however, that the energy difference between different surface reconstructions was found in all theoretical studies to be of the same order as the precision of the calculations themselves.³² Hence, as far as the theory is concerned, the ground state dimer configuration for this surface is still a matter of debate.

The controversy about the origin of the $p(2 \times 1)$ phase of the Si(001) surface has been recently addressed in a combined theoretical and experimental study.³³ In this work a noncontact AFM (NC-AFM) experiment conducted at 5 K at small frequency shifts demonstrated a characteristic zig-zag pattern of bright spots in the images proving conclusively that the $c(4 \times 2)$ phase is the ground state of this surface. At larger frequency shifts corresponding to the tip coming much closer to the surface during its vertical oscillations, a sym-

metric $p(2 \times 1)$ structure was observed. Using *ab initio* DFT calculations it was shown, however, that this effect is caused by the direct tip-surface interaction which results in frequent flipping of surface dimers by the tip when it is in the proximity of lower atoms of dimers. Thus, at large frequency shifts and low temperatures the AFM tip manipulates surface dimers (see also Ref. 34) leading to a permanent deformation of the surface. At small frequency shifts and low temperatures the NC-AFM does not change the dimers orientation and thus can be used to “read out” the surface structure before and after an intrusive experiment.

Note that NC-AFM images of the Si(001) surface have not yet been simulated using an *ab initio* method; in fact, theoretical studies of the interaction of AFM tips with this surface are quite scarce. In Ref. 35 an *ab initio* DFT method was used to study the response of the surface when a Si dangling bond terminated tip was moved laterally across the dimer perpendicular to the dimer row. The induced dimer flip was also found in tight-binding calculations³⁶ in which a smaller Si tip was approached vertically above the lower atom of the dimer. In this case the force on the tip was found to be different for approach and retraction, with the dimer flip only observed if the tip comes below some critical distance to the surface. This type of hysteretic behavior, characteristic for dissipation effects,^{37–43} was found above the upper dimer atom as well, although in a lesser extent; a dimer flip did not happen in this case. Using simulated force-distance curves on a lateral grid, the authors of Ref. 36 obtained NC-AFM images of the Si(001) surface for the cases of a weak tip-surface interaction, i.e., when the tip does not go beyond the critical distance at which the dimers start to flip. These simulations indicated that the upper dimer atoms are imaged as bright, and the NC-AFM image of the $c(4 \times 2)$ surface has a characteristic zig-zag pattern.

In this paper we shall consider the theoretical modelling, based on an *ab initio* DFT method, of the NC-AFM images of the Si(001) surface. Not only a wide range of temperatures will be covered in this study, but also various frequency shifts corresponding to tip-surface interaction ranging from weak to very strong. The peculiar feature of flipping dimers, characteristic for this surface, presents a challenge for the theory, and we shall show how one can construct topography NC-AFM images of this surface taking into account both the thermal motion of surface atoms (i.e., dimer flipping) and the intrusive character of the tip-surface interaction at close approach. We also discuss in much more detail than in Ref. 33, how the orientation of dimers on the surface can be forcefully changed (manipulated) using specific tip scan directions.

This paper is organized as follows: The *ab initio* method we use here is briefly outlined in Sec. II. The Si tip initiated dimer flipping³³ is summarized in Sec. III. We also consider in this section if the surface can “heal” itself during the time of a single tip oscillation. The NC-AFM topography images at various temperatures are discussed in Sec. IV. The main results of this study are summarized in Sec. V, where we also suggest, in the spirit of Refs. 34 and 33, manipulation experiments at very low temperatures that should allow predefined dimer orientations on the surface to be created and observed.

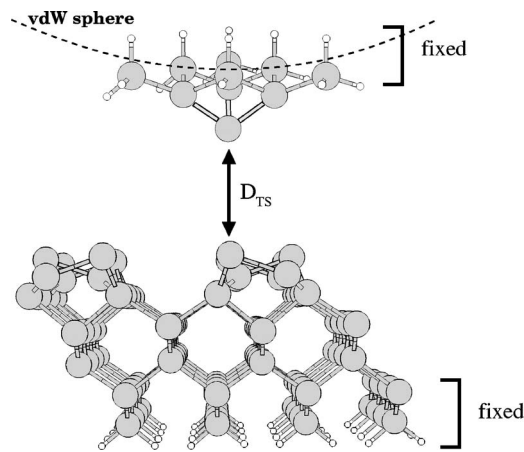


FIG. 1. The Si cluster modelling the tip above a surface dimer. The distance between the tip and surface, D_{TS} , and the sphere position used to model the van der Waals force (Ref. 60), are explicitly indicated.

II. METHOD

In most of our calculations we used an *ab initio* DFT method as implemented in the SIESTA (Ref. 44) code. Calculations with SIESTA were performed using the GGA Perdew-Burke-Ernzerhof (PBE) (Ref. 45) and LDA Perdew-Wang (PW92) (Ref. 46) density functionals. The SIESTA code utilizes periodic boundary conditions, norm-conserving pseudopotentials, and a localized numerical basis set to describe the valence electrons. A standard double-zeta polarized basis set is chosen for this study which for Si gives 13 orbitals to describe the valence electrons with a maximum orbital size of 6.9 Bohr radii. In some cases SIESTA calculations were backed up by VASP (Refs. 47 and 48) calculations to check the issue of the localized basis set. All VASP calculations were performed solely using the GGA paw-PBE functional, the energy cutoff for the plane wave basis set was 300 eV for Si.

A 6-layer slab model with 16 silicon atoms per layer (8 dimers arranged in two rows with 4 dimers each) is used to describe the surface. Hydrogen atoms are used to terminate the dangling bonds on the lower side of the slab and thus to simulate the missing bulk. A single $\mathbf{k}=0$ (Γ point) is used in all calculations due to the large size of the simulation cell. During preliminary calculations the hydrogen atoms at the bottom of the slab were allowed to relax while all Si atoms were fixed in their bulk positions. In all subsequent calculations (e.g., when calculating a dimer flip and the force-distance curves above various lateral positions within the cell) the hydrogen atoms together with the two bottom layers of silicon atoms were fixed, while all other atoms of the surface were allowed to relax.

A Si tip was used in the NC-AFM experiments^{7,33} on the Si(001) surface. Any contamination on the tip apex was removed by Ar-ion sputtering, so it is plausible that there was a dangling bond at the tip apex. This is modelled in our simulations by a ten Si atom tip saturated at its base by 15 hydrogen atoms. This tip model, as shown in Fig. 1, has been used extensively in other simulations^{49,50} and has a diffuse dangling bond protruding from its apex. The positions of the

hydrogen atoms at the upper layer of the tip and of the four Si atoms at its bottom were found in a separate calculation on an isolated tip in which the upper layer of Si atoms were fixed in their bulk positions. Then the positions of the hydrogen atoms and silicon atoms in the uppermost layer were fixed throughout all simulations. The vertical distance between the tip and surface is measured between the lowermost tip (apex) atom and the upper surface dimer atom *prior* to atomic relaxation as indicated in Fig. 1. In all SIESTA calculations the vacuum gap was kept large (~ 14 Å) to prevent unphysical interactions between adjacent slabs.

Note that the multiple calculations necessary to simulate NC-AFM images for this system were carried out with SIESTA, as it would have been prohibitively expensive to use VASP for this purpose. To satisfy ourselves as to the precision of the SIESTA calculations for this system, we first studied the three main reconstructions of the Si(001) surface, namely $c(4 \times 2)$, $p(2 \times 2)$, and $p(2 \times 1)$ asymmetric, with both codes. The energy differences per dimer between the different configurations and geometrical characteristics of the dimers are summarized in our previous paper.⁵¹ The results obtained for both the energy and the geometry with SIESTA and VASP are in good agreement with the previous theoretical study of this system.⁵² In particular, we confirm that the two surfaces with the “antiferromagnetic” ordering, $p(2 \times 2)$ and $c(4 \times 2)$, are lower in energy than the $p(2 \times 1)$ configuration, with a very small preference towards the $c(4 \times 2)$ structure.

The results obtained for the Si(001) surface with the localized basis set are very similar to those obtained from the plane wave VASP calculations, indicating that the basis set we use in the SIESTA calculations is appropriate for our purposes.

III. TIP-SURFACE INTERACTION AND A DIMER FLIP

In this section the interaction between the Si tip and an individual surface dimer considered previously for the $c(4 \times 2)$ surface in Ref. 33, is summarized. In addition, we describe similar simulations performed for the $p(2 \times 1)$ surface. At certain conditions the tip-surface interaction results in the dimer flipping and the issue of whether or not the dimer will return to its ground state after the flip, which is relevant for the interpretation of NC-AFM topography images, is also discussed.

A. Approach-retraction force-distance curves above a Si dimer

In order to study the tip-surface interaction the tip is initially positioned with its apex atom ~ 7 Å directly above the lower and upper atoms of a surface dimer. The geometry of the composite system is then optimized before the tip is moved vertically downwards towards the surface in steps of 0.15 Å. At every step the system is allowed to relax using the SIESTA method until the forces on the non-fixed surface and tip atoms are no larger than 0.02 eV/Å. After the lower turning point was reached, the tip was then moved upwards in the same way. The tip force was calculated at each quasi-static step in the simulation by summing the individual

forces on all the fixed tip atoms. This method has been shown to give reliable values for the chemical force when used in other systems.^{53,54} Through this procedure both the approach and retraction tip-surface force curves have been obtained.

The results of our calculations for both the $p(2 \times 1)$ and $c(4 \times 2)$ surfaces can be summarized as follows. When the tip is positioned above the upper dimer atom, an attractive tip force is developed and at a distance of $D_{TS} \approx 3.8 \text{ \AA}$ a chemical bond starts to form between the upper dimer and the tip apex atom. Further approach of the tip induces the dimer into a symmetric configuration. Upon retraction, the sequence of events repeats itself in the reverse order, the bond between the two atoms eventually being broken as the tip moves far away from the surface. The atomic relaxation mirrors itself for the approach and retraction and this results in identical force distance curves for approach and retraction above this site, with no hysteresis observed. This is contrary to the results of the previous tight-binding calculations³⁶ that observed a small force hysteresis above this site.

A strikingly different result is obtained when the tip is positioned above the lower dimer atom. Once again upon approach an attractive force is felt. At a distance around $D_{TS} \approx 3.6 \text{ \AA}$ (which is sensitive to the actual lateral position of tip with respect to the lower dimer atom) the tip apex atom forms a chemical bond with the lower dimer atom causing the dimer to flip, the actual distance between the two atoms drops sharply by about 1.0 \AA . This effect has already been reported in a previous tight-binding study of this surface.³⁶ The tip and surface remain bonded as D_{TS} is further reduced inducing the dimer into a symmetric configuration. Upon retraction, the situation becomes almost identical to that above the upper atom: the tip remains chemically bonded to the dimer atom until a critical separation is reached, whereupon the bond is broken. The important effect is that the dimer can be flipped by the tip approaching the lower dimer atom and remains in a flipped state after the tip is retracted. This can however only happen if the tip comes closer than a certain critical distance so that to enable the formation of the chemical bond between the tip apex and the lower dimer atoms.

To summarize, a scan above the lower dimer atom in which the tip approaches close enough to flip the dimer will result in a permanent deformation of the surface at very low temperatures, with the dimer unable to flip back upon the retraction of the tip. As a result of this behavior, the tip force-distance curves are different above the lower dimer atom for approach and retraction. A characteristic hysteresis behavior is observed with the tip force on retraction lying below that on approach. It is important to emphasize here that the hysteretic behavior of the force will only occur if the tip comes closer than the critical distance mentioned above; otherwise, the retraction curve will follow exactly the same route as it did on approach.

Thus, we find in general a qualitative agreement with earlier *ab initio* calculations^{34,35} in which the tip formed a bond with the nearest Si dimer atom and, if this atom happens to be the lower dimer atom, a dimer flip was induced. A similar observation was made in Ref. 36 in which vertical force-distance curves were calculated using a simpler electronic

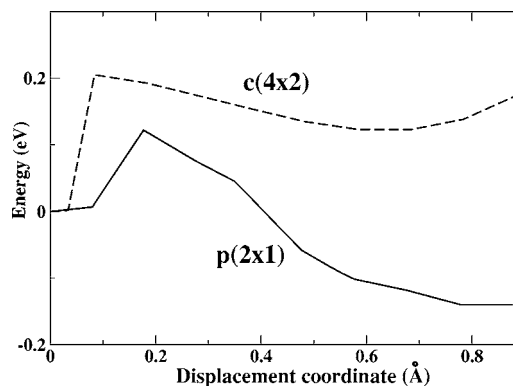


FIG. 2. Calculated potential energy surfaces of a single dimer to flip and flip back on the $p(2 \times 1)$ and $c(4 \times 2)$ surfaces. Zero value of the coordinate (the horizontal axis) corresponds to the dimer ground state.

structure method. Contrary to their tight-binding work, we find no hysteresis when the tip is oscillated above the upper dimer atom. The hysteretic behavior is observed only when the tip is positioned laterally in close proximity to the lower dimer atom.

B. Dimer flip

It follows from the results of the previous section that imaging above a *lower* dimer atom could result in a permanent damage to the surface. To understand why a continuous imaging of this surface is possible, it is necessary to estimate a barrier for the dimer, that has been flipped by the tip, to flip back to its original orientation. If, at a given temperature, the probability is high for the dimer to return spontaneously to its initial position within the time taken for the cantilever to perform a single oscillation, then this same process will be continually repeated for subsequent oscillations. In other words, by the time the tip approaches the surface again, the latter can manage to “heal” itself via thermal motion. If this is not possible, then the dimer will remain in the flipped position for every subsequent tip oscillation, i.e., the initially lower dimer atom will be imaged in practice as an upper one. This point shall be revisited in Secs. IV and V.

The forward and backward energy barriers needed to flip an individual surface dimer have been estimated using SIESTA. This was done using a constrained energy minimization method in which the upper atom of a *flipped* dimer was displaced vertically downward in quasistatic steps of 0.1 \AA ; this induces the dimer to flip back and the surface to recover its equilibrium state. The upper atom vertical position was fixed at each step, although it was allowed to relax within the surface plane (i.e., laterally). At every step the positions of all other surface atoms were optimized until the forces were reduced to less than 0.01 eV/\AA . A surface cell containing 8 dimers was used in these calculations.

The transition energy paths for the dimer to flip for both the $c(4 \times 2)$ and $p(2 \times 1)$ configurations calculated as described above are shown in Fig. 2. The energies and vertical displacements are shown relative to those corresponding to the ground states for the two reconstructions.

Note that the total energy of the system is lowered when a $p(2 \times 1)$ surface dimer is flipped. This is because, according to our DFT calculations, this particular reconstruction is not the ground state of the Si(001) surface, where dimers prefer alternating orientations corresponding to the “antiferromagnetic” ordering. Thus, when a dimer is flipped, energy is actually gained. The ground state $c(4 \times 2)$ surface with a single flipped dimer is about 0.12 eV higher in energy than the ground state, which is in agreement with other DFT slab calculations.^{15,55} The energy barrier that is necessary to overcome a flipped dimer to flip back (i.e., in order for the surface to rediscover its ground state configuration) is 0.08 eV for the $c(4 \times 2)$ reconstruction and 0.26 eV for the $p(2 \times 1)$ reconstruction. To initially flip a dimer from its ground state configuration an energy barrier of 0.2 eV for $c(4 \times 2)$ and 0.12 eV for $p(2 \times 1)$ needs to be overcome. It should be noted that a constrained energy minimization approach tends to overestimate energy barriers, hence these should be taken as upper limits. In other studies⁵⁵ a symmetric dimer was taken to be the saddle point, while in Ref. 15 the barrier was estimated by varying the buckling angle between the upper and lower dimer atoms. However, energy barriers of the same order of magnitude were obtained.

Thus, a barrier of ~ 0.2 eV is needed to flip a single dimer on the $c(4 \times 2)$ surface, however, a much smaller barrier of 0.08 eV is only needed for the dimer to restore its original orientation. The implication of these results is that one can recognize three temperatures in this system: low, intermediate, and high (the detailed breakdown will be given at the end of this section). At low temperatures T dimers are thermally frozen, i.e., they cannot flip between the two configurations. At intermediate T the dimers still cannot flip thermally from the ground state. However, if flipped by an external force (e.g., by the tip), they can thermally flip back restoring the ground state configuration. At high T all dimers can freely thermally flip back and forth.

There are two relevant questions one has to address in order to be able to simulate NC-AFM images of the Si(001) surface taking into account the dimers flipping ability: (i) what is the characteristic time for a dimer to flip back after it was flipped by the tip at a given T , and (ii) what is the distribution of flipped dimers in the surface at the same temperature. In principle, both these questions can be answered using a statistical mechanics treatment, for example, by applying a model Ising Hamiltonian that describes the interplay between various dimers configurations across the surface.¹⁹ Then, to simulate the dimer flip-back time, one may use a kinetic Monte Carlo (MC),⁵⁶ to calculate the distribution of the dimers in the surface at equilibrium—an equilibrium MC simulation.^{57,56} Since such calculations go beyond the scope of this study, we shall instead employ a much simpler model calculation.

To estimate the time that would be required for the dimer to flip back, we consider a simple first order kinetics of the dimer backward flip. Let $p_2(t)$ be the probability of finding the dimer in the flipped state. The rate of change $\dot{p}_2(t) = -p_2/\tau$, where the transition rate $\tau^{-1} = \nu_2 e^{-\Delta_2/k_B T}$ with Δ_2 being the energy barrier to flip back and ν_2 is the corresponding prefactor. Since $p_2(0) = 1$ (the dimer is initially in the flipped

state), we get $p_2(t) = e^{-t/\tau}$. Estimates for the characteristic time τ required for the dimer to flip can be done by assuming that the barrier $\Delta_2 \approx 0.1$ eV, as in our calculations, and $\nu_2 \sim 10^{13} \text{ s}^{-1}$. From this it follows that at temperatures $T \geq 70$ K the time τ is smaller than the tip oscillation period $T_{\text{osc}} \approx 10^{-5}$ s.

This means that at rather low temperatures (smaller than ~ 70 K), any dimer once flipped will most probably remain flipped by the time the tip approaches the dimer again at the next oscillation. In other words, the lower dimer atom will be imaged as the upper one since it appears as the upper atom after the dimer is flipped during the first tip oscillation above this site. Then, during the subsequent tip oscillations the dimer will remain in the flipped state, i.e., the used to be lower dimer atom will be on average imaged as an upper one. No dissipation is to be expected in this case as all, but one of the tip oscillations are not hysteretic.

At higher temperatures, the dimer will be able to flip back fast enough, so that at each oscillation the tip will be able to image it as a lower atom. In this case each oscillation will be hysteretic, and the dissipation energy (per cycle) as estimated from the hysteresis loop in our calculations is found to be about 0.3 eV.

The above treatment should only be valid at not very high temperatures, i.e., well below the phase transition temperature of 200 K, since around and above this temperature many dimers start to behave *collectively*⁵⁵ and our estimate of the energy barrier becomes invalid. Still, even in this case, one can consider an average, “effective” dimer sitting in a double-well potential with the barriers Δ_1 and Δ_2 ($\Delta_1 > \Delta_2$) and the prefactors ν_1 and ν_2 , where state 1 corresponds to the ground and 2 to the flipped state. If n_1 and n_2 are the equilibrium populations of the two states in the surface, $n_1 + n_2 = 1$, then from the detailed balance equation, $n_1 \nu_1 e^{-\Delta_1/k_B T} = n_2 \nu_2 e^{-\Delta_2/k_B T}$, we can estimate the two populations as

$$n_1 = \left(1 + \frac{\nu_1}{\nu_2} e^{-\Delta/k_B T} \right)^{-1}, \quad (1)$$

$$n_2 = \left(1 + \frac{\nu_2}{\nu_1} e^{\Delta/k_B T} \right)^{-1}, \quad (2)$$

where $\Delta = \Delta_1 - \Delta_2$ is the energy difference between the flipped and the ground states. Note that the populations correspond to probabilities to find a single dimer in either of the states at given T .

This simple result has the correct qualitative behavior, namely that at small temperatures $n_2 \approx 0$, while at large T the populations n_1 and n_2 , assuming $\nu_2/\nu_1 \approx 1$, both approach $\frac{1}{2}$. However, one cannot use in this formula the value of $\Delta \approx 0.1$ eV as calculated above for the $c(4 \times 2)$ structure, as this value is based on the calculation in which only a single dimer was flipped. The value of Δ can be estimated in such a way as to give a sharp increase in n_2 around the temperature of the phase transition, $T_c = 200$ K, when the collective effects start to dominate. Assuming $\nu_2/\nu_1 \approx 1$, and using Eqs. (1) and (2), one then finds that the desired behavior of the

populations can be obtained if $\Delta \approx 0.01$ eV. This rather small value reflects a collective behavior of the dimers in this surface at large temperatures.

Concluding this section, three temperature intervals are to be introduced in the cases when it is essential to take account of the dimers flipping (e.g., large frequency shifts): (i) *low* ($T \leq 70$ K), (ii) *intermediate* ($70 \text{ K} \leq T \leq 200$ K), and (iii) *large* ($T \geq 200$ K).

IV. SIMULATING NC-AFM IMAGES OF THE Si(001) SURFACE

A. Calculating the frequency shift

The interaction between the AFM tip and surface can be split¹² into two components: (i) the microscopic chemical force between atoms in the tip and the surface, that in this work was calculated using the *ab initio* SIESTA method as explained below, and (ii) the macroscopic force. The latter force for this system is the attractive van der Waals (vdW) force (in some cases electrostatic forces should also be considered.^{58,59}).

The macroscopic force does not depend on the lateral position of the tip. It is well-known¹² that it is only the short range chemical forces that are responsible for the atomic scale contrast in the NC-AFM images. The macroscopic forces are nevertheless important in order to reproduce experimentally obtained frequency shifts for a particular system and can be treated as an attractive background force.

In this work we assumed a conical tip with the angle $\gamma = 30^\circ$ and a sphere of the radius $R = 100$ Å and used an expression derived by Argento *et al.*⁶⁰ for the vdW force, see also Fig. 1. The Si-Si Hamaker constant of $H = 1.865 \times 10^{-19}$ J determined experimentally in Ref. 61 has been used in our calculations.

To model the chemical interaction between the tip and sample for a given lateral position of the tip, DFT calculations have been performed for a set of vertical tip-surface distances as explained in Sec. III. The macroscopic vdW force is then added to the microscopic chemical force to give the complete force $F_{ts}(z)$ as a function of tip-surface distance z . The resonance frequency of the oscillating cantilever is then calculated according to the well-known expression^{62,12}

$$\left(\frac{\omega}{\omega_0}\right)^2 = 1 - \frac{1}{A\pi k} \int_0^{2\pi} F_{ts}(z_0 + A \cos \phi) \cos \phi d\phi, \quad (3)$$

where $F_{ts}(z)$ is the total tip-surface force consisting of the micro and macroscopic contributions, $\omega_0 = 2\pi f_0$ is the resonant frequency of the cantilever at infinite separation, k is the cantilever spring constant, and A is the oscillation amplitude. z_0 is the average height about the surface of the oscillating cantilever. For our simulations all necessary parameters have been taken from an experimental study of this surface by Uozumi *et al.*⁷ and are as follows: $k = 40$ N/m, $f_0 = 160$ kHz, and $A = 100$ Å.

This method allows for the dependence $\omega(z_0) = 2\pi f(z_0)$ of the resonance frequency on the average tip position z_0 to be calculated at the given lateral tip position. Then, for the given frequency shift $\Delta f = f - f_0$, the value of z_0 is determined.

To construct an AFM image, the tip is positioned over many points on the surface, a lateral two-dimensional mesh of points is built up, where at each site force and frequency curves are calculated and the value of z_0 is obtained. For both the $c(4 \times 2)$ and $p(2 \times 1)$ surfaces, rectangularly shaped irreducible parts of the surface unit cells were identified in which evenly spaced lateral grids of points were chosen with a separation in the directions along and perpendicular to the dimer rows of 0.75 Å and 0.65 Å, respectively. Force curves were produced above each individual site and it was found that for the majority of cases these were for all purposes identical upon the approach and retraction of the tip, with the exception being only sites around and above the lower dimer atom.

As it follows from the consideration in Sec. III, one has to be rather careful when analyzing the response of the Si(001) surface to the tip oscillations during the NC-AFM experiments. It is necessary to define two regimes for the tip-surface interaction: (i) a weak one corresponding to rather small frequency shifts when dimers are not flipped by the tip and (ii) a strong one corresponding to large frequency shifts when they are. In principle, an intermediate regime is also possible,³³ however, we shall not consider it here. The effects of large and small frequency shifts within several temperature regions are discussed in the forthcoming sections.

B. Weak tip-surface interaction

If the frequency shift is *small*, the tip never comes close enough to the surface in order to flip the dimers. Only the phase transition temperature is of essence here as the reference point when dimers can flip by themselves. Thus, one may consider the following *three* temperature intervals:

(1) *Low* and *intermediate* temperatures ($T \ll 200$ K).

In this case the dimers cannot flip thermally from the ground state. Hence, upper atoms should be imaged as bright, while lower atoms (if visible) as dim. The image is weakly dependent on T , as the number of dimers in ground state, $n_1(T)$, given by Eq. (1), is approximately equal to unity in this temperature range.

(2) *Near phase transition* temperatures ($T \sim 200$ K).

At these conditions the dimers start to experience a flip-flop motion. Therefore, there will be a statistical distribution of flipped dimers according to Eqs. (1) and (2). The upper and lower atoms of the surface dimers will appear as bright and dim spots; however, the image will now depend strongly on T , with the difference in contrast between the two spots becoming reduced with increasing T .

(3) *Large* temperatures ($T \gg 200$ K). The dimers readily undergo a flip-flop motion, hence on average there will be equal amounts of dimers in either state. The upper and lower atoms will appear in the image as equally bright spots. The dependence of the image on T in this temperature range is not expected to be significant.

In all three cases no dissipation is to be expected as dimers are not flipped by the tip and hence its motion is purely conservative.

To simulate the NC-AFM image at a given temperature T , we consider a careful selection of lateral grid points within

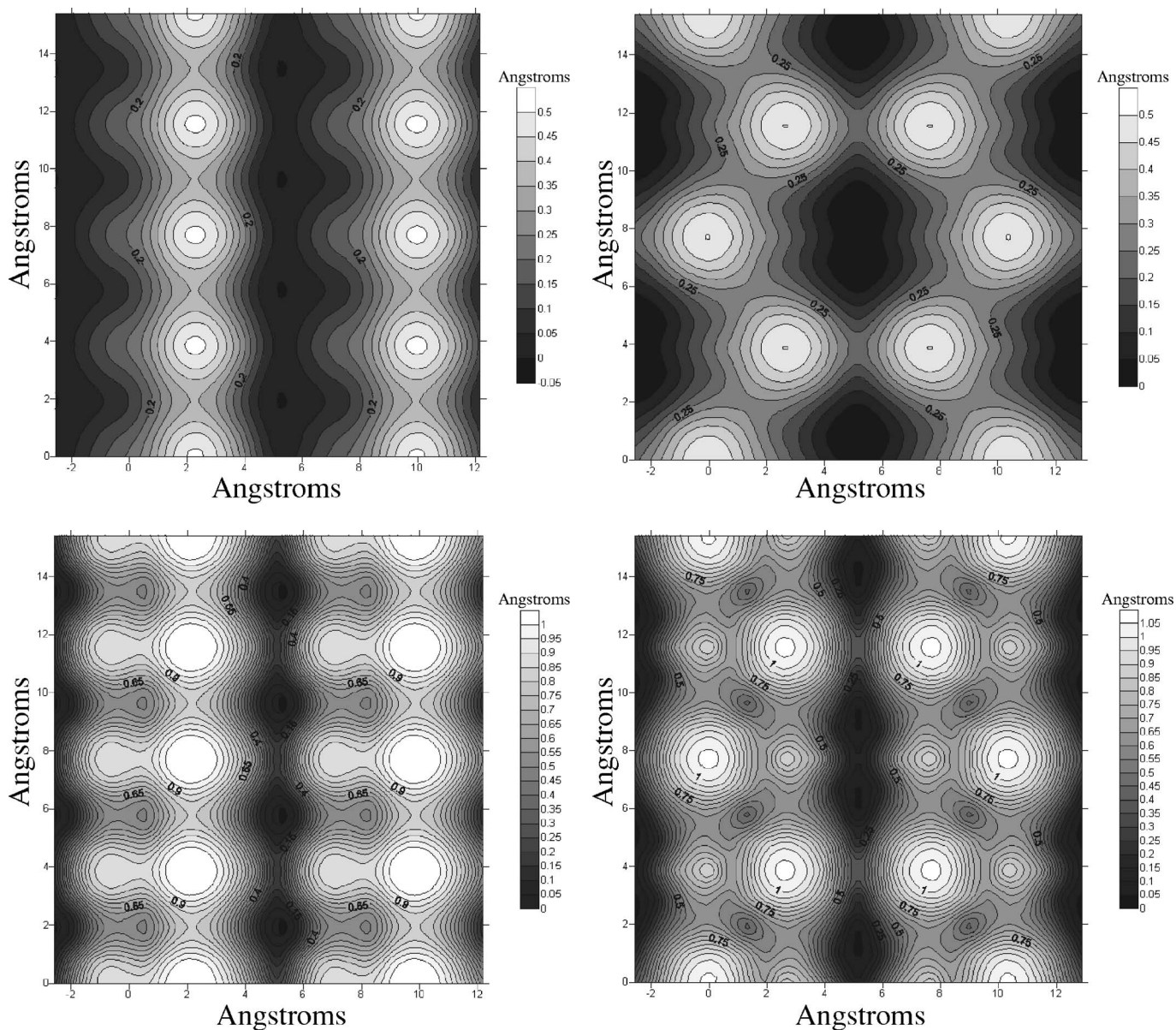


FIG. 3. Simulated low temperature NC-AFM images of the $p(2 \times 1)$ (left) and $c(4 \times 2)$ (right) reconstructions of the Si(001) surface ($T=0$ K in actual calculations). Top panels correspond to the frequency shift $\Delta f = -20$ Hz, bottom panels to $\Delta f = -32$ Hz.

the unit cells of the two reconstructions, $c(4 \times 2)$ and $p(2 \times 1)$, as explained above. Let $F_{ts}^{\text{grnd}}(x, y, z)$ and $F_{ts}^{\text{flip}}(x, y, z)$ be the tip-surface force fields with the dimer in its ground and flipped states for the given reconstruction. Then, the NC-AFM image of the dimer can be obtained from Eq. (3) by using the weighted force field

$$F_{ts}(x, y, z) = n_1(T)F_{ts}^{\text{grnd}}(x, y, z) + n_2(T)F_{ts}^{\text{flip}}(x, y, z) \quad (4)$$

with the dimer state population functions given by Eqs. (1) and (2). The populations show the fraction of oscillation cycles during the tip residence time the dimers are in either of the states.

In order to calculate the force field $F_{ts}^{\text{flip}}(x, y, z)$, one has to flip a single dimer and then calculate the force field by placing the tip at different lateral and vertical positions with re-

spect to it (as for a surface *defect*). This calculation would be extremely time consuming. Instead, the force field $F_{ts}^{\text{flip}}(x, y, z)$ was obtained approximately by “reflecting” the calculated ground state force field $F_{ts}^{\text{grnd}}(x, y, z)$ across the dimer center. Note that it was assumed here that the tip force is mostly sensitive to the dimer underneath the tip; the influence of the neighboring dimers is less important. This assumption seems to be reasonable as our calculations show that the tip forces above lower (upper) atoms of dimers taken from either $c(4 \times 2)$ or $p(2 \times 1)$ surface reconstructions are quite similar.

Low temperature topography images of the $c(4 \times 2)$ and $p(2 \times 1)$ surface reconstructions obtained for frequency shifts of $\Delta f = -20$ Hz and $\Delta f = -32$ Hz are shown in Fig. 3. At the lower frequency shift one can see the upper dimer atom is clearly imaged, while the lower atom is not seen at all. The

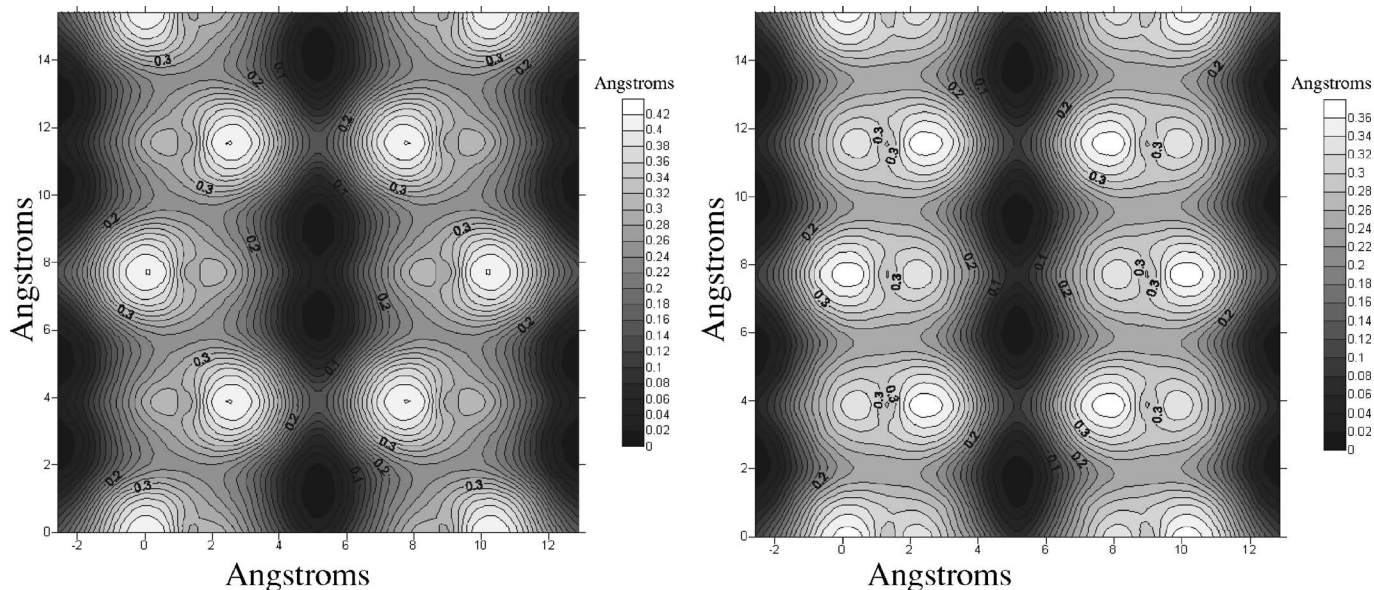


FIG. 4. Simulated NC-AFM images for the $c(4 \times 2)$ reconstruction of the Si(001) surface at a frequency shift of -18 Hz at finite temperatures 100 K (left) and 350 K (right).

$p(2 \times 1)$ configuration is imaged with the bright spots arranged along a straight line, while the $c(4 \times 2)$ reconstruction demonstrates a clear zig-zag pattern characteristic for this particular configuration's arrangement of dimers.^{7,8} To image the lower atom as well, one has to approach the surface closer, i.e., increase the frequency shift Δf . It is possible to achieve this without coming so close that a bond is formed with the tip Si apex atom and the dimer is induced to flip. The calculated low temperature images at $\Delta f = -32$ Hz that are shown in Fig. 3 clearly demonstrate this point. As before, the upper dimer atom is clearly imaged; however, this time the lower atom is partially visible as a separate maximum of lower intensity.

As was mentioned above, as the T increases the two atoms should be imaged as bright spots of similar intensity. This is demonstrated for the $c(4 \times 2)$ reconstruction in Fig. 4 where the topographic images were calculated at $T = 100$ K and 350 K. If in the former case the lower dimer atom is still easily distinguishable from the upper one on the image, at $T = 350$ K the two atoms are imaged almost equally.

The calculated images demonstrate clearly that at weak tip-surface interaction (i.e., relatively small frequency shifts) and small temperatures, it should be possible to recognize the surface reconstruction without altering the arrangements of surface dimers. Although we have not considered the $p(2 \times 2)$ structure here, it is obvious from the results above that the characteristic in-phase zig-zag pattern of this particular reconstruction should be clearly distinguishable from the out-of-phase zig-zag pattern of the $c(4 \times 2)$ and straight stripes of the $p(2 \times 1)$ reconstruction. Therefore, the NC-AFM, at least with Si-terminated tips, should be able to image different various surface reconstructions without modifying the surface, a clear advantage over the STM based methods where the tip-induced surface reconstruction (by surface charging) cannot be ruled out.¹⁰

C. Strong tip-surface interaction

For *larger* frequency shifts (i.e., stronger tip-surface interactions), when the tip at its lowest turning point comes closer

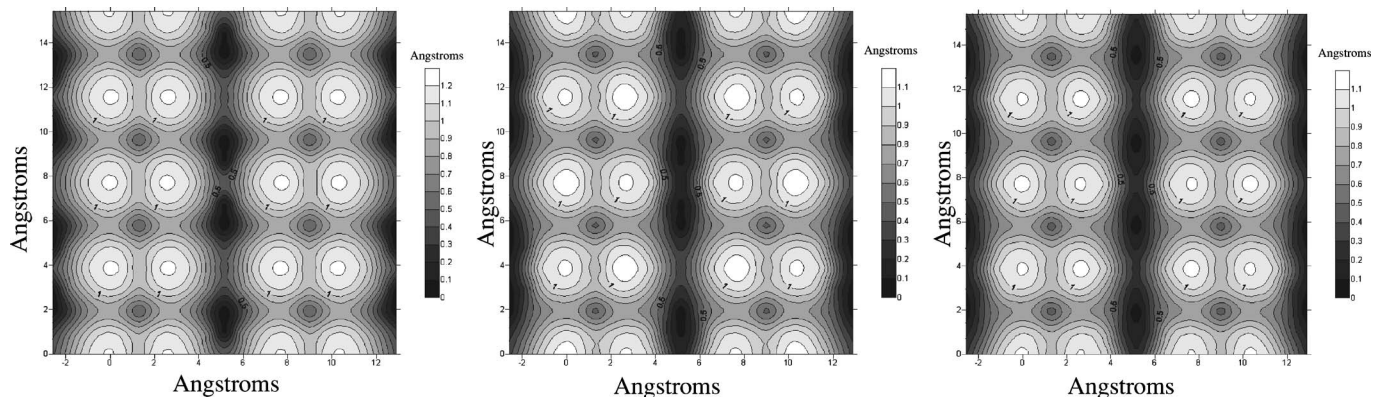


FIG. 5. Simulated NC-AFM images for the $c(4 \times 2)$ reconstruction of the Si(001) at a frequency shift of -40 Hz in the strong interaction regime. The temperature from left to right: 0 K, 100 K, and 350 K.



FIG. 6. (Color online) Schematic of dimers flipping after a single scan above a row of alternating dimers of an original $c(4 \times 2)$ structure shown in (a). Low temperatures and large frequency shifts are assumed. The red dashed line indicates the scan direction. In (b), dimers that changed their direction once are shown in green, while those that changed their directions twice in red. At the end of the scan, red dimers remain in their original state, whereas green dimers flipped. Lower and upper dimer atoms are shown with the small black and large open circles, respectively.

than the critical distance necessary for the dimers to be flipped (Sec. III B), another set of *three* temperature regions should be distinguished as discussed at the end of Sec. III B:

- *Low* temperatures ($T \leq 70$ K). If the tip flips a dimer when oscillating near its lower atom, the dimer will remain in the flipped state upon retraction and subsequently for all other oscillations above this point. Hence, both lower and upper atoms should be imaged as upper (bright) and no dissipation should be observed. In practice, depending on the scan speed (and thus the average number of tip oscillations above a given lateral position, i.e., the residence time), some weak damping signal may be seen and the brightness of the two dimer atoms in the topography image may not be completely identical (one may appear slightly dimmer). Note also, that the image will depend on the way in which the scan is performed as discussed in more detail in Sec. IV. In summary, at these conditions, the NC-AFM tip will modify the surface and the particular sequence of dimer flips will depend on the way the lateral displacement of the tip is performed. Since both dimer atoms are to be imaged as bright, the surface topography image should correspond to the symmetric $p(2 \times 1)$ phase in complete agreement with the experiment.³³

- *Intermediate* temperatures ($70 \text{ K} \leq T \leq 200 \text{ K}$). In this case the ground state dimers are still frozen; however, if a dimer is flipped by the tip, it will thermally be able to return to its ground state by the time the tip returns again at the next oscillation. Therefore, lower atoms will be imaged dimmer than the upper ones, since on approach (during half of the tip oscillation) they are further away from the tip. In the damping image, however, lower atoms should appear as bright (the image reversed) with the estimated dissipation energy per cycle of 0.3 eV (see Sec. III). No surface modification is to be expected at these imaging conditions.

- *Large* temperatures ($T \geq 200 \text{ K}$). Since dimers can easily flip-flop, each dimer atom will be imaged equally bright. At the same time, the probability of finding a dimer atom as a lower one when the tip is approaching is also approximately equal to $\frac{1}{2}$ for the two dimer atoms so that both atoms should equally experience flipping caused by the tip. Therefore, a damping image should be observed with equal brightness for the two dimer atoms. Note, however, that on average

only half of the tip oscillations during its residence time would result in dimer flips, so that corrugation in the damping image is expected to be halved as compared with the previous case with $E_{\text{diss}} \approx 0.15$ eV per cycle. Some temperature dependence is also expected near the transition temperature of 200 K.

The NC-AFM images for large frequency shifts and low temperatures can be simulated essentially by adopting the following approximate approach. Since in this case each dimer atom behaves as an upper one, the dimer image can be constructed out of the half associated with the upper atom that is now “mirrored” to the lower atom part. In essence, it means that each dimer has an additional symmetry mirror plane cutting it in two identical halves. An image of the $c(4 \times 2)$ surface simulated in this way is shown on the left panel in Fig. 5. It can be seen that at very low temperatures it is impossible to distinguish the lower and upper atoms, i.e., the surface appears as the $p(2 \times 1)$ phase in agreement with the recent NC-AFM images.³³

The simulation of the topography images at intermediate and large T can be done using the same method. Each dimer has probabilities $n_1(T)$ and $n_2(T)$ of being in its ground and flipped states, respectively. Therefore, the force field can be calculated using the same method as in Sec. IV B; in particular, Eq. (4) should be used. The only difference with the method of the previous section is that the average force on approach and retraction should be used in the present case.⁶³ This is, however, important only for those lateral tip positions that are above and around the lower dimer atom, when a hysteresis is observed. The image will depend on T , especially around the phase transition temperature. As an example, we show in Fig. 5 images of the $c(4 \times 2)$ surface calculated in this way at $T = 100$ K (middle) and 350 K (right panel). One can see that at high temperatures both atoms look very similar. However, some difference in contrast is observed at an intermediate temperature.

V. DISCUSSION AND CONCLUSIONS

The calculations demonstrate that for relatively small frequency shifts (i.e., at weak interactions where the surface is not deformed) it is possible at low temperatures to clearly

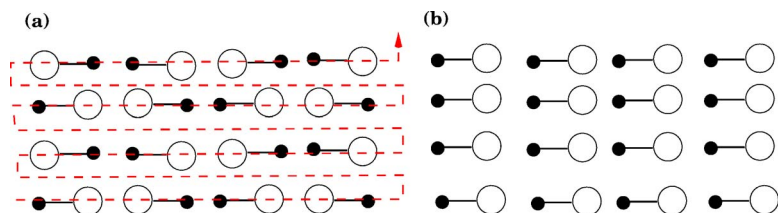


FIG. 7. (Color online) A schematic showing how the $c(4 \times 2)$ structure (a) can be transformed into the $p(2 \times 1)$ one (b) by applying a special scan protocol shown by a dashed red line. Lower and upper dimer atoms are shown with the small black and large open circles, respectively.

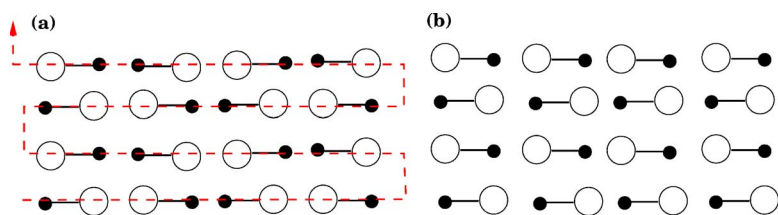


FIG. 8. (Color online) A schematic showing how the $c(4 \times 2)$ structure (a) can be transformed into the $p(2 \times 2)$ one (b). Notations are the same as in Fig. 7.

resolve both the upper and lower dimer atoms as two local maxima with different intensities. This allows the surface reconstruction to be unambiguously identified. For the particular case of $p(2 \times 1)$ a set of bright spots arranged in straight lines along the dimer rows will be observed, while for $c(4 \times 2)$ a zig-zag formation of bright spots along the dimer rows will be seen, with the lines on adjacent rows running in antiphase to each other. Although we have not specifically considered the $p(2 \times 2)$ surface in this study due to the cost of the *ab initio* calculations to be involved, it is evident from our results that the $p(2 \times 2)$ surface should be represented by bright spots along zig-zag lines running *in-phase* with each other. Thus, the imaging regime in question can be used to identify the particular surface reconstruction without modifying its structure by a strong tip-surface interaction. This is in sharp contrast to the STM based techniques that are believed to be intrusive when applied to this surface even at low temperatures (due to the charging effects).¹⁰

Our calculated NC-AFM images at small frequency shifts and low T for the $c(4 \times 2)$ reconstruction, see right panels in Fig. 3, agree remarkably well with the experimental one acquired at 5 K and $\Delta f = -10$ Hz.³³ In both images the characteristic zig-zag pattern of bright spots corresponding to the $c(4 \times 2)$ reconstruction is evident. This means that the $c(4 \times 2)$ structure is indeed the ground state of the Si(001) surface.

Images calculated at large temperatures with the same small frequency shifts show that both dimer atoms become almost indistinguishable, making it impossible within the weak interaction regime to determine the surface reconstruction. Hence, only NC-AFM experiments conducted at low temperatures ($T \gtrsim 70$ K) and in the weak interaction regime can be used to *probe* the surface as the dimer arrangement should be apparent in the topography image.

The situation at larger frequency shifts when the tip comes sufficiently close to the surface to induce a dimer flip (above lower dimer atoms) is more complex. If experiments are conducted at low temperatures, dimers are permanently

flipped by the tip during the imaging process; every time the tip passes a dimer, it leaves *the last imaged atom* frozen as the upper one, see a schematic illustration in Fig. 6. Therefore, this particular regime can be used to *manipulate* the surface reconstruction. A possible manipulation experiment (the idea of manipulating surface dimers with a tip was first suggested in Ref. 34) can be conducted as follows. Initially, using a low temperature and a small frequency shift, one can scan the surface to identify its structure. Then, a larger frequency shift set point is set, and the oscillating tip is moved along a particular direction across the surface or is made to perform back and forth swipes according to a certain algorithm, “writing” a particular arrangement of surface dimers. By retracting the tip to the initial set point of the frequency shift and scanning the surface again, the new arrangement of dimers after the manipulation can be verified (“read out”).

Possible scan protocols that can turn the $c(4 \times 2)$ structure into the $p(2 \times 1)$ or $p(2 \times 2)$ reconstructions are shown in Figs. 7 and 8, respectively. A more complex restructuring can be achieved by employing more complicated scanning protocols as illustrated in Fig. 9.

In conclusion, we have simulated, entirely from the theoretical viewpoint, the NC-AFM images of the Si(001) surface in the constant frequency shift mode for various temperatures. We show using an *ab initio* calculated force field and a Si tip with a single dangling bond, that at rather low frequency shifts and very low temperatures, it must be possible to image the surface without imposing any permanent modification, so that this particular regime can be used to determine the current dimers arrangement; an AFM tip serves as a soft probe. By setting a larger frequency shift set point, the tip may come very close to surface dimers and flip them according to the way it is moved laterally across the surface. This regime, implemented to some level of sophistication, could be used to manipulate surface reconstruction at will. By retracting the tip from the surface (e.g., to the original frequency set point), one can then scan the modified surface to check its status after the manipulation.

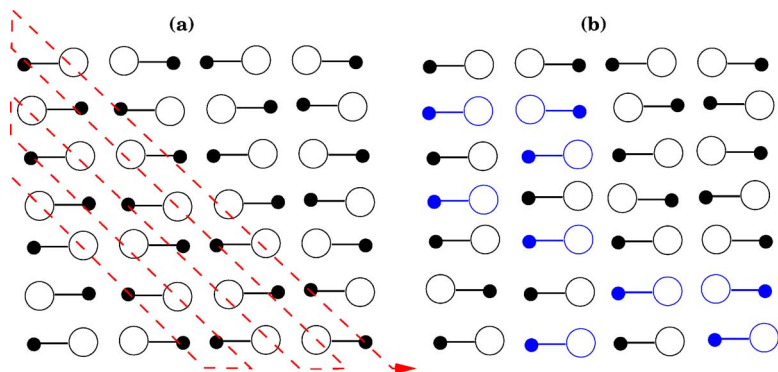


FIG. 9. (Color online) A transformation of dimers of the $c(4 \times 2)$ structure shown in (a) into a more complicated structure (b) obtained by performing a finite number of scan lines (dashed red lines) at an angle to the dimer rows. Dimers affected by the procedure are shown in (b) in blue.

There should be no dissipation observed if scanning either at low frequency shifts or large frequency shifts and low temperatures.

We also discussed how the topography image should depend on temperature, and suggested how it can be calculated. It is shown that at high temperatures (larger than the phase transition $T_c=200$ K), both dimer atoms should be imaged as almost equally bright due to free thermal flip-flop dimer motion. At larger frequency shifts and the same T , dissipation effects should also take place with the damping image being similar to the topography one, dissipated energy per cycle $E_{\text{diss}} \approx 0.15$ eV. We also note that one may think that freely flipping dimers at $T > T_c$ may produce some contribution to the stochastic friction force^{64–66} and hence to the dissipation energy. Indeed, every flipping dimer may be modelled as a single oscillating “pseudoatom.” However, from our experi-

ence, we anticipate that this contribution should be much smaller than the above mentioned energy of adhesion caused by the tip induced dimer flipping.

Much larger dissipation, $E_{\text{diss}} \approx 0.30$ eV per cycle, and thus increased corrugation in the damping image should be observable within some intermediate range of T . The damping image for these conditions is predicted to be inverted with respect to the topography; while the upper atoms in the topography images being the brightest, the lower atoms should be brightest in the damping images.

Unfortunately, only a limited amount of experimental NC-AFM data is available at present.^{7,8,33} Further experimental studies are necessary to be carried out at a range of temperatures and frequency shifts in order to test fully the predictions from our theory.

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