Toggling Bistable Atoms via Mechanical Switching of Bond Angle

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We reversibly switch the state of a bistable atom by direct mechanical manipulation of bond angle using a dynamic force microscope. Individual buckled dimers at the Si(100) surface are flipped via the formation of a single covalent bond, actuating the smallest conceivable in-plane toggle switch (two atoms) via chemical force alone. The response of a given dimer to a flip event depends critically on both the local and nonlocal environment of the target atom—an important consideration for future atomic scale fabrication strategies.

The bistability inherent in a number of atomic and molecular systems provides a natural route towards the development of (sub)nanoscale switching devices. Since the seminal atomic switch demonstration of Eigler *et al.* [1], single atom or molecule switching has been realized in a diverse set of adsorbate-substrate systems [2–8]. In each case switching was electronically actuated via, for example, modification of junction resistance, inelastic tunneling, resonant injection of electrons into a specific molecular orbital, or, most recently, adatom charging.

Here we introduce a new approach to switching at the atomic level which involves the toggling of one or more bistable atoms via the making and breaking of a single covalent bond. Although dynamic force microscopy has been used of late to perform a variety of elegant atomic manipulation processes [9–12], the ability to toggle bond angle at the single atom limit represents a fundamentally new mode of control, enabling modification of local geometric and electronic structure without the need to deposit, remove, or laterally displace surface atoms.

The bistable unit we exploit for our experiments is a nonplanar (buckled) silicon dimer—the fundamental building block of the reconstructed Si(100) surface [13–15]. Si(100) has hitherto been exploited for a number of scanning tunneling microscope (STM)-driven switching experiments [2,16], and silicon dimer-based memory and logic schemes have also been proposed [17–19]. Tunneling electrons produce a significant long-range interaction [19] and so appear to preclude the ability to controllably target and flip individual dimers with atomic precision. Li *et al.* [20] demonstrated that it was possible, by altering the tip-surface interaction, to modify the Si(100) surface reconstruction observed in dynamic force microscopy images. This addressed the controversy regarding the influence of scanning probes on the Si(100) ground state but enticingly left open a key issue: is it possible to manipulate Si(100) on a dimer-by-dimer basis?

In this Letter we show, by operating a noncontact atomic force microscope (NC-AFM) (Omicron Nanotechnology) under zero applied bias conditions at 5 K and in the qPlus mode introduced by Giessibl [10,21], that although single dimers can indeed be mechanically flipped between buckled configurations, the dynamics of flipping sensitively depend not only on the local but on the nonlocal environment.

Figure 1(a) shows the results of a typical manipulation experiment. First, we operated in frequency shift mode (i.e., Δf feedback) at low set point, observing buckled dimer rows forming a $c(4 \times 2)$ phase. We then positioned the tip over the "down" atom of a dimer, switched off the feedback loop, and moved the tip closer to the sample while measuring the frequency shift; i.e., a Δf-vs-z spectrum was acquired. At a certain tip-sample distance a sharp jump is observed in the Δf signal, and on the subsequent retraction the Δf-vs-z curve differs strongly from the approach spectrum. This jump in the value of Δf, coupled with the hysteretic behavior, is the signature of a change in the tip-sample interaction due to a dimer flip. It arises when the chemical force reaches the threshold required to destabilize the dimer—the target atom then jumps into contact with the tip, resulting in a switch of the intradimer bond angle from $\sim +19°$ to $-19°$. Subsequent imaging using the same scan parameters showed a change in the local dimer configuration from a $c(4 \times 2)$ phase to a phason pair structure [22].

We highlight that when the initial configuration is the $c(4 \times 2)$ phase we cannot flip individual dimers to form a "three-in-a-row" structure, where three consecutive dimers have the same buckled orientation. Only *correlated* flipping is observed for a starting $c(4 \times 2)$ configuration. Having generated the phason pair shown in Fig. 1(a) we then flipped the dimer back to its initial state, recovering the original $c(4 \times 2)$ configuration [Fig. 1(b)]. A comparison of Fig. 1(a) with Fig. 1(b) shows that the threshold Δf value, and thus the tip-sample interaction force, required to
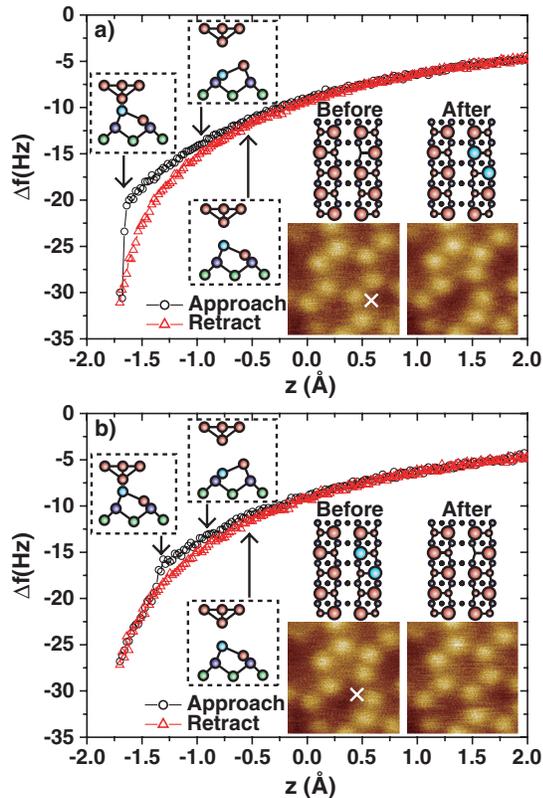
FIG. 1 (color online). Toggling silicon dimers. (a) Open circles: Frequency shift (Δf) measured as a function of tip displacement (z) towards the "down" atom of a Si(100) dimer. Open triangles: Δf-vs-z spectrum acquired during retraction of the tip. The insets show NC-AFM images, and illustrations of the atomic configurations, taken before and after the frequency shift measurement (acquired at the position marked with a cross). The dimer flipping event appears as a sharp jump in the Δf-vs-z spectrum. (b) A Δf-vs-z spectrum taken above a "down" atom of one of the phasons created in (a) restores the original symmetry via a second correlated flip event. (Image parameters: tip amplitude, 250 pm; Δf set point = -9.1 Hz)

remove phason pairs is lower than that required to inject phasons.

Phasons also form naturally on Si(100) [and the structurally similar Ge(100) surface] [22,23], and their diffusion can be induced either thermally or through local excitation [19,24]. Parallels with spin-flip excitations in the context of an Ising chain were explored by Pennec *et al.* [19] who indirectly monitored the (biased) random walk of a phason via tunnel current fluctuations. Figure 2 illustrates that, in the absence of excitation due to tunneling electrons, it is possible to drive deterministic phason motion with single atom precision via "spin" flips excited by NC-AFM.

In order to determine, from the Δf-vs-z data, the strength of the covalent interaction required to flip dimers, it is essential to accurately remove the long-range (van der Waals and electrostatic) contribution [10,12,25]. The approach we have adopted involves measuring Δf-vs-z spectra in pseudoconstant height mode on different terraces close to an atomic step edge [26]. The variation
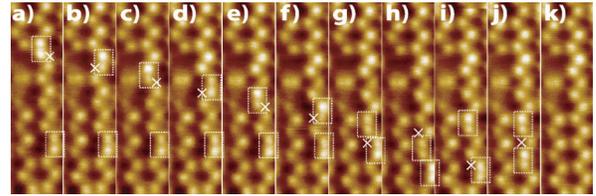

FIG. 2 (color online). Manipulating and annihilating phasons. The two "native" phasons highlighted in (a) are moved via controlled dimer flipping until they annihilate via the flip event shown in (j) to produce the region of $c(4 \times 2)$ symmetry in (k). In (a)–(g) the upper phason is sequentially moved down the dimer row via a succession of single dimer flip events (generated in each case by a single Δf-z spectrum taken at the position marked by the cross). (A movie of the induced phason motion is available online [26].)

of the short-range tip-sample force with distance from the surface (the F-z spectrum), Fig. 3, was then evaluated from the background-corrected Δf-vs-z spectra via application of the Sader-Jarvis inversion algorithm [27]. Figure 3 also includes the short-range (i.e., covalent) tip-sample interaction calculated using density functional theory for two types of tip structure: a (111)-type termination and a dimer-terminated cluster [26]. We used the SIESTA code [28] with a double-zeta polarized basis set giving 13 orbitals to describe the valence electrons on every silicon atom. Calculations were performed with the generalized gradient approximation Perdew-Burke-Ernzerhof density functional and norm-conserving pseudopotentials. Typically, atomic relaxation was considered complete when forces on atoms were not larger than 0.01 eV/Å.

In Fig. 3 we compare the experimental F-z curves with the calculated spectra for a flip from a standard zigzag buckled configuration to a phason pair state [Fig. 3(a)] and back again [Fig. 3(b)]. In each case, during the approach of the tip there is a sharp increase in the magnitude of the force when a certain threshold is reached, indicating that the dimer has flipped. The lack of any change in the dissipation signal indicates both that the tip in this case [26] is structurally rigid and that the dimer flip event, occurring as it does during a single tip oscillation period, is associated with a negligible average energy loss per cycle.

First, we consider the retract F-z curves, which arise from the interaction of the tip with the "up" atom which has been switched from a "down" atom during the approach curve. Independent of the choice of tip type in the density-functional theory (DFT) calculations, there is excellent agreement between experiment and theory for the F-z spectra acquired above "up" atoms, providing strong evidence that the spectroscopic and manipulation data we have acquired arise from the formation of a single covalent bond between tip and sample.

Comparison between experiment and theory for the approach spectra is rather more complicated. DFT predicts that both the tip type and the configuration of neighboring dimers can affect the threshold force required for a

flip [26]. Although Δf-vs-z spectra clearly illustrate the influence of the configuration of neighboring dimers on the threshold force (Fig. 1), we find the error bars associated with the determination of the short-range force from the Δf-vs-z data are of same order as the difference predicted by DFT [26]. Nonetheless, on the basis of multiple manipulation events, we can state that the force required to flip a dimer is significantly less than 1 nN, falling in the range 100–600 pN.

Although the experimental and DFT force-distance curves are in good qualitative agreement, there is an important and striking difference between experiment and simulation in Fig. 3. While DFT predicts the formation of a (meta)stable three-in-a-row configuration [Fig. 4(a), position iii], this structure has not once been observed in experiment. In order to reconcile the DFT calculations with experiment, the potential energy surface and associated energy barriers for dimer flipping must be considered. We used the nudged elastic band (NEB) method [26] to explore the energy landscape associated with transitions between dimer flip configurations in the presence and absence of the tip. Figure 4(a) shows the minimum energy

pathways predicted by the NEB technique for a transition from a $c(4 \times 2)$ structure to a phason pair configuration, as a function of tip-sample separation.

The set of energy bands plotted as open triangles in Fig. 4 illustrates that the minimum energy pathway to form a phason pair requires the formation of an intermediate three-in-a-row configuration. Although the barrier to the three-in-a-row state (position iii) collapses as the tip is brought closer to the "down" atom of the central dimer, a significant barrier—thermally insurmountable at 5 K—is *always* present for the transition to the phason pair state (position iv), regardless of tip-sample separation. Barrier lowering due to the presence of the tip [29] alone therefore appears to be insufficient to explain our experimental data. Moreover, any proposed mechanism should not only explain our ability to inject (and remove) phason configurations, it must also elucidate why a relatively high percentage of flip events *do not* produce a permanent change in dimer configuration, with the system returning to a $c(4 \times 2)$ structure during retraction of the tip [30].

The potential energy landscape shown in Fig. 4 provides a simple explanation for these "flip-but-flip-back" events. If the system remains trapped in the three-in-a-row state at the closest approach of the tip, the barrier to return to the $c(4 \times 2)$ state effectively vanishes as the tip is retracted. The experimental observation that the system can routinely cross the barrier to the phason pair configuration is less straightforward to explain. One issue that we explored extensively using molecular dynamics simulations [26]
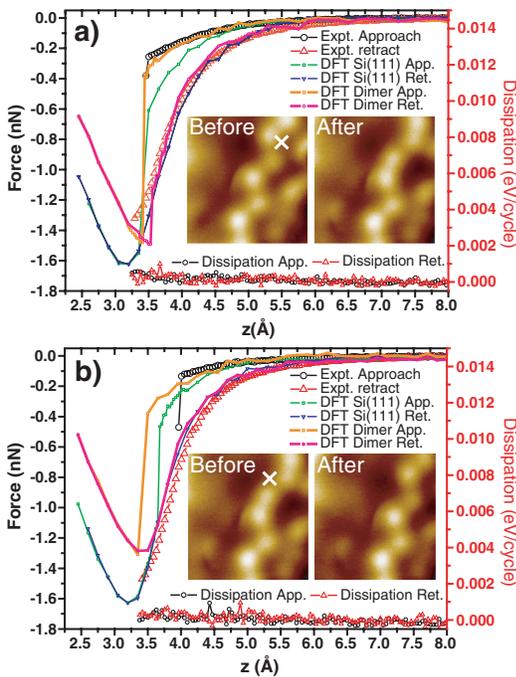

FIG. 3 (color online). Measuring the force required to flip a dimer. (a) Open circles (triangles): Variation of the short-range force during tip approach (retraction) at the position marked with a cross in the "before" image. Note that it is not strictly valid to use the Sader-Jarvis algorithm [27] to plot the short-range force beyond the "discontinuity" due to the dimer flip and so we show only one force point (for clarity) beyond this threshold. Also plotted is the negligible variation in dissipation (for this tip [26]). The DFT-calculated spectra (solid lines), while in excellent agreement with experiment for the retraction curves, show that the threshold force at which the flip occurs is critically dependent on tip structure. (b) As for (a) except that the tip restores the original zigzag buckling.
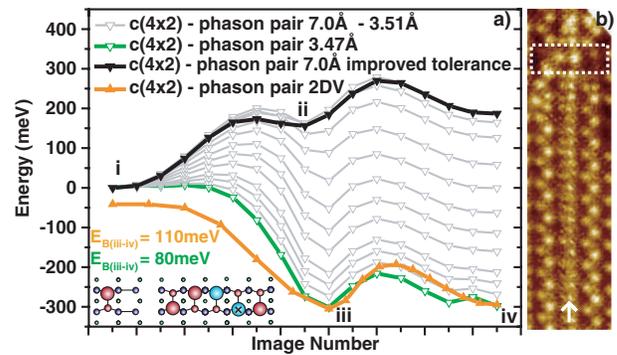

FIG. 4 (color online). (a) Energy profile associated with the transition from a $c(4 \times 2)$ structure (position i) to a phason pair configuration (position iv) for a range of tip-sample separations. As the tip-sample separation is decreased ($\triangledown$), the barrier for the transition to an intermediate three-in-a-row state (positions ii and iii)—never observed in experimental images—collapses ($\triangledown$). As the tip retracts, the barrier between the three-in-a-row and $c(4 \times 2)$ states decreases dramatically ($\blacktriangledown$). Introduction of a two-dimer-vacancy (2DV) defect produces the energy band shown as ($\blacktriangle$) (offset for clarity) at the closest tip approach. *Part* of the 2DV computational cell is shown in the inset (see [26] for more detail). (b) Long-range influence of a defect on the barrier for dimer flipping. In the row highlighted with an arrow, dimers appear symmetric while neighboring rows are clearly buckled. Image taken at 77 K; $\delta f = -40$ Hz; amplitude = 100 pm; $V_{gap} = 10$ mV.

was the role of the ~300 meV of energy injected into the lattice due to the relaxation of the system to the three-in-a-row configuration. The amount of energy transfer (at the *pristine* surface) is, however, insufficient to surmount the 80 meV barrier to the phason pair state—a maximum of ~10 meV of kinetic energy is delivered to each dimer neighboring the target ''down'' atom [26]. Figure 4(b) and previous STM work [24,31], however, provide compelling experimental evidence that defects dramatically influence the energy barriers for dimer flipping.

To examine the extent to which the energy landscape is modified, we introduced a double dimer vacancy defect [see inset of Fig. 4(a)] and repeated the NEB calculation for the smallest tip-sample separation [orange curve in Fig. 4(a)]. The defect changes the barrier to the phason pair state by almost 40% (from 80 to 110 meV). It is clear that other defects [including boron-induced ad-dimers [32], Fig. 4(b)] can tilt the energy balance in the other direction, *reducing* the barrier. Modeling the influence of a boron-derived defect on the energy surface, however, represents a significant theoretical challenge. Nonetheless, the NEB and DFT calculations shown in Fig. 4 clearly demonstrate that the presence of defects, and the associated long-range coupling to dimers in their vicinity, governs the flip dynamics observed in our experiments.

The results described here demonstrate that it is possible to routinely and reversibly switch bond angle via a short-range covalent tip-sample interaction. Not only does this represent a new atomistic switching and manipulation protocol, enabling the direct, in-plane, mechanical control of bistable atoms, but our data provide key insights into the role of local correlations and nonlocal influences in setting the limits on our ability to manipulate matter at the atomic level.

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