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Interplay between Switching Driven by the Tunneling Current and Atomic Force of a Bistable Four-Atom Si Quantum Dot

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Supporting Information

ABSTRACT: We assemble bistable silicon quantum dots consisting of four buckled atoms (Si_4-QD) using atom manipulation. We demonstrate two competing atom switching mechanisms, downward switching induced by tunneling current of scanning tunneling microscopy (STM) and opposite upward switching induced by atomic force of atomic force microscopy (AFM). Simultaneous application of competing current and force allows us to tune switching direction continuously. Assembly of the few-atom Si-QDs and controlling their states using versatile combined AFM/STM will contribute to further miniaturization of nanodevices.



KEYWORDS: Atomic manipulation, atomic switch, Si quantum dot, scanning tunneling microscopy, noncontact atomic force microscopy, density functional theory

ver the last two decades, tremendous effort has been expended in the pursuit of new functional nanoscale devices.¹ Achieving this goal will depend on our ability to fabricate nanostructures that can be reversibly switched in a controlled manner. The smallest realizations of the switches typically consist of molecules or surface atoms evolving between stable configurations. Most of the present switching mechanisms employ electronic excitation using scanning tunneling microscopy (STM).²⁻¹³ However, only a few mechanical switches using noncontact atomic force microscopy (NC-AFM) have been realized.^{14–16} Here we show that the combination of tunneling current (STM) and atomic force (AFM)^{17–20} provides new possibilities for switching the atomic configuration of nanostructures. First we use atomic manipulation to engineer a bistable silicon quantum dot (QD) consisting of four buckled atoms on the Si(111)-7 \times 7 surface. We show that application of the current and the force induces the opposite downward and upward movement of an atom (see Figure 1) located under a tip apex accompanied by conformational changes of the whole Si₄-QD. This allows us to perform controlled switching between different states of the Si-QD by the tunneling current and/or the atomic force. Moreover, simultaneous application of the current and force allows us to

tune the switching rates. We believe that the selective application of two different mechanisms will open new horizons for the development of nanoscale switching devices or atomic manipulation.

There is a strong demand from the semiconductor community to keep the leading position of the silicon technology in the future. This will require, among other advances, the further miniaturization of Si-based nanodevices. Thus, the possibility of forming the Si₄-QD and controlling its states represents a singular opportunity. The Si₄-QD adopts a buckled rhombus with two equivalent stable conformations, denoted left (L) and right (R) according to the orientation of the two upper atoms. A vertical change of one of four atoms leads to rearrangement of the remaining atoms and consequently to switching between the L and R conformations. Thus, the system provides an ideal model for investigating the atomistic switching mechanism on a well-defined semiconductor structure.

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Figure 1. Schematic view of different switching processes leading to different atomic contrast of the Si₄-QD. (a, b) Atomic structure, STM contrast and schematic drawing of the left (L) and right (R) conformation of Si₄-QD, which can be switched either (c) downward by current or (d) upward by force. (e) Alternatively, switching rates can be tuned via the interplay between the two mechanisms. (f, g) Different nontrivial atomic contrasts obtained during scanning in the STM or AFM modes, respectively.



Figure 2. Atom-by-atom assembly of Si₄-QD and mirror-symmetric bistable conformations of the Si₄ atom switch. (a, b) Sequential STM images ($V_s = -1.5 \text{ V}$, $I_t = 0.05 \text{ nA}$, T = RT) showing the assembly of Si₄-QD from Si₁ by atom manipulation.¹⁷ Black dotted triangles indicate Si₁ diffusing in a half unit cell of Si(111)-7 × 7. Si₄ is fabricated at the center of a unit cell indicated by a solid rhombus by gathering the scattered Si₁, as indicated by the arrows. (c, d) STM images of mirror-symmetric L and R conformations of Si₄ atom switching as indicated by the dotted square (1.0 nm × 1.0 nm) at the center of Si(111)-7 × 7 unit cells indicated by a solid rhombus ($V_s = -0.5 \text{ V}$, $I_t = 0.1 \text{ nA}$, T = 80 K). UH and FH denote the unfaulted and faulted halves of Si(111)-7 × 7 unit cells, respectively. The mirror-symmetric line is indicated by the solid line between (c) and (d). (e, f) Corresponding simulated constant-current STM images of Si₄ atom switch for L and R conformations, respectively (dotted square: 1.0 nm × 1.0 nm). All balls indicate Si atoms. U and D denote the up and down positions of Si atoms of Si₄-QD. U atom on FH: UFH (green); U atom on UH: UUH (red); D atom on FH: DFH (black); D atom on UH: DUH (blue). The lateral atom distance between U atoms is 3.8 Å as indicated by a narrow. The vertical heights of U atoms from D atoms are 0.5 and 0.7 Å for the unfaulted and faulted halves, respectively. (i) Contour plot of the calculated HOMO state localized at U atoms of L-Si₄. (j) Calculated DOS at each Si atom showing the HOMO and LUMO states.

Here we take advantage of the recent progress in scanning probe microscopy, which enables simultaneous detection of the tunneling current and force on the atomic scale.^{17–20} We show that the tunneling current (STM) between the tip and the upper Si atoms of the Si₄-QD causes a downward movement of the Si atoms (Figure 1c). On the other hand, the atomic force (AFM) induces an upward movement of lower atoms of the Si₄-QD (Figure 1d). Even tuning of the upward and downward switching rate is possible using combined STM/AFM (Figure 1e). In addition, the proper choice of image mode (STM or AFM) and feedback condition (bias voltage and/or tip–sample

distance) allows selective encoding of four different configuration states.

We formed the Si₄-QD using atom manipulation at room temperature (RT).²¹ Figure 2a and b show the sequential atomby-atom assembly process of the Si₄-QD on the Si(111)-7 × 7 surface (see Figure S1). In this manipulation process two extra Si atoms are deliberately moved into the same Si(111)-7 × 7 unit cell, where they spontaneously form an Si₄-QD structure with two native center adatoms of the Si(111)-7 × 7 surface. This process is very reproducible, and it allows the formation of identical Si_n-QDs with well-defined atomic and electronic structures, thereby eliminating any statistical variations in their



Figure 3. Current-induced downward atom switching. (a) Schematic drawing showing the bright area of Type-R Si₄. (b–k) Bias dependence of the filled-state STM images of Si₄ atom switching (V_{si} (b) -0.450 V, (c) -0.500 V, (d) -0.550 V, (e) -0.575 V, (f) -0.600 V, (g) -0.625 V, (h) -0.650 V, (i) -0.700 V, (j) -0.800 V, (k) -1.00 V, $I_t = 0.1$ nA, 1 mm × 1 nm, T = 80 K). Arrows in (c) indicate the fast and slow scan direction of a raster scan of the STM tip. Dotted lines in (c) indicate the scan lines at which atom switching occurs between L and R. The circle in (g) indicates numerous switches where a darker area is dominant, meaning that downward switching occurs preferentially. (l) Schematic drawing of cross Si₄ which is an intersection (L∩R) of bright area of Type-L and R Si₄. (m) Log–log scale I_t dependence of the atom switching rate (R) measured above each Si atom position of the Si₄ atom switch (up atom on the faulted half; UFH (green square), up atom on the unfaulted half; UUH (red inverted triangle), down atom on the faulted half; DFH (black circle), down atom on the unfaulted half; DUH (blue triangle)) ($V_s = -0.63$ V). Solid lines indicate fitting results for identifying the power N of $R = I^N$. Insets exhibit time dependence of I_t measured by fixing STM tip height above the center of bright protrusion of Si₄ on faulted half. I_U and I_D indicates I_t of U and D Si atom state, respectively. τ_U indicates the lifetime of the U state. (n) Schematic view of the potential energy surface and relevant parameters describing the electron switching mechanism; (o) sequential STM images ($V_s = -0.35$ V) showing continuous controlled downward switching. By applying pulse high bias ($V_s = -0.6$ V, 5 s) above the center of the up state Si atom (black dot) of Si₄, it switches to the down state.

size and shape (see Figure S2 and Movie S1). Here, we employed Si₄-QD as a symmetric bistable switch to be used in place of the asymmetric frozen Si5-QD and Si6-QD (see Figure S2 and Movie S1). Figure 2c and d show filled-state STM images of two mirror-symmetric conformations of Si₄-QD acquired at low bias voltages and 80 K. We observe the characteristic diagonal bright protrusions located at the center of the Si(111)-7 \times 7 unit cell. We corroborated the atomic and electronic structure of the Si4-QD using the total energy density functional theory (DFT) calculations²² and STM simulations²³ (see Methods for details). We identified two equivalent ground state L and R conformations, consisting of mirror-symmetric rhombus-arranged Si atoms as shown in the models in Figure 2g and h. The atomic structure is formed by two diagonal Si atoms (blue and black in Figure 2g) with only weak chemical bonding to each other and located in the in down position (denoted by D), while the two outer diagonal Si atoms (red and green in Figure 2g) remain in the upper position (denoted

by U) and are slightly buckled. However, the Si_4 -QD is covalently bounded to the Si substrate. From the simulated STM images shown in Figures 2e and f, we can assign the bright protrusions to two U atoms. The local density of states (LDOS), plotted in Figure 2j, shows two electronic states at 0.5 V below and above the Fermi level, which are strongly localized on the Si₄-QD. Thus, they can be considered as frontier HOMO and LUMO orbitals of the Si₄-QD due to their weak electronic coupling with other surface and bulk states.

At a temperature of 80 K the Si₄-QD remains quenched in one of the ground state conformations (either L or R). Spontaneous thermally activated switching between these two conformations is prevented due to a presence of an activation energy barrier $E_{\rm b} \sim 0.44$ eV, as determined using the nudged elastic band method (NEB) (Figure S9).^{22,24} The transition between the two ground states L and R occurs via a concerted flip-flop motion of the buckled Si₄ (Movies S2 and S3). This is similar to the flipping of buckled Si dimer rows on the Si(001)



Figure 4. Force-induced upward atom switching. (a–e) Sequential frequency shift (Δf)-dependence of NC-AFM images of the Si₄ atom switch (Δf ; (a) –3.7 Hz, (b) –3.7 Hz, (c) –3.8 Hz, (d) –3.9 Hz, (e) –4.1 Hz, $V_s = 0.0$ mV, 1 nm × 1 nm, T = 80 K). U in (a) and (b) denotes an Si atom in the up position. Dotted lines in (c) indicate scan lines in which atom switching occurs between L and R. (f) Schematic drawing of square Si₄ which represents the union (LUR) of the bright areas (U state) of L and R Si₄. (g) Experimental and simulated short-range force-dependence on z during tip approach (blue) and retraction (red), with the tip initially positioned above the D state Si atom (blue) of the Si₄-QD on the unfaulted half. Insets show a snapshot of the Si₄ and tip before and after upward atom switching. (h) Sequential (from left to right) schematic images showing the Si₄ states and tip position, as indicated by black dots, and acquired Δf -z curves on the position. When the tip is positioned above the U state atom, the Δf -z curve shows switching as indicated by the black arrows.

surface.^{4,5,15} Nevertheless, we should note that there is an important difference with respect to the Si(001) dimers. The motion and the electronic structure of individual Si dimers on Si(001) is strongly coupled to those of the nearest neighbor dimers. This is not the case for Si₄-QD, which can be considered a four-atom cluster that is electronically very weakly coupled to the substrate. Hence the Si₄-QD can be considered as the ultimate realization of bistable Si-QDs.

First, we describe the controlled switching of the Si₄-QD between the L and R conformations, which is exclusively driven by the electron excitation using the STM tunneling current. Figure 3b-k represents a series of constant current STM images acquired with increasing bias voltage at 80 K (see also Figure S3). We used a small current set point of 0.1 nA to exclude any mechanical interaction between the tip and the sample. STM images acquired at -0.45 V show a stable Si₄-QD located in the R state (schematically drawn on Figure 3a). However, during scanning at a slightly elevated bias of -0.50 V, switching between the L and R conformations was observed, as indicated by the dotted lines in Figure 3c. This bias energy matches the energy of the HOMO state determined by the DFT calculations (see Figure 2j). Therefore, we attribute the switching mechanism to the resonant electron tunneling from the HOMO state to the tip.

The switching frequency increases rapidly with the applied bias voltage. The switches occur tens of times during the scan of one image, indicating the presence of lateral linear noise (Figure 3d-f). At a bias above -0.6 V, switching occurs several times even in a single scan line (Figure 3g-i). Finally, when the bias voltage exceeds -0.80 V, the switching rate becomes larger than the acquisition time of a single pixel (0.50 ms/pixel), and the switching noise is no longer detected due to the limit of the experimental bandwidth, as shown in the STM images presented in Figure 3j and k. The STM images display the Si₄-QD as a characteristic bright cross-shaped form ("cross Si₄"

hereafter). This characteristic cross shape results from the intersection of STM images of the L and R-states, as depicted schematically in Figure 3l.

Note that the area corresponding to one Si atom of the Si₄-QD, indicated by the white circle in Figure 3g, is imaged as a dark dip instead of a bright protrusion. This means that the lifetime of the upper (brighter) atom position is much shorter than that of the lower (darker) atom position. In other words, the average effect of the tunneling current is to push the Si atoms in the up (U) position to the down (D) position, meaning that downward switching occurs preferentially. This allows us to selectively commute between the L and R states in a controlled way as shown in Figure 3o, where 10 alternating L–R switches are performed.

To shed more light on the STM switching mechanism, we analyzed the time evolution of the tunneling current I_t . We kept the tip positioned at a fixed height above the center of the bright protrusion of a Si₄ atom for different bias voltages with the feedback loop off. The I_t time evolution shows typical telegraph noise spectra with two well-defined extremes of I_D and I_U (see the inset of Figure 3m), which correspond to the down (D) and up (U) positions of the Si atom, respectively. The spectra shown in Figure 3m reveal that the averaged lifetime $\langle \tau_D \rangle$ of an Si atom in the down position is much longer than the average lifetime of an atom in the Up position $\langle \tau_U \rangle$ with a residence ratio $\langle \tau_D \rangle / \langle \tau_U \rangle$ of ~25. This confirms that the downward switching is strongly preferred in the STM mode.

Next, we analyzed the dependence of the downward switching rate $(R_{U\rightarrow D} = 1/\langle \tau_U \rangle)$ and the upward switching rate $(R_{D\rightarrow U} = 1/\langle \tau_D \rangle)$ on the tunneling current I_t . Figure 3m plots on a log-log scale the I_t dependence of *R* measured above each Si₄-QD state on the faulted (FH) and unfaulted (UH) half. We found that all rates *R* increase linearly with I_p i.e., $R \propto I_t^N$ with $N \approx 1$ (see Figure S4). This demonstrates that the electronic switching mechanism is a one-electron process.²⁵



Figure 5. Interplay between current-induced downward switching and force-induced upward switching at Si₄-QD. (a–f) Sequential I_t -dependence of STM images; $I_t = (a)$ 14 nA, (b) 10 nA, (c) 8.0 nA, (d) 6.0 nA, (e) 2.0 nA, (f) 1 pA with $V_s = -0.65$ V at 80 K. (g–i) Time dependence of I_t measured by fixing the tip height above the center of the bright part of Si₄ at 80 K. (j) Tip–sample distance (z)-dependence of $R_{D\rightarrow U}$ (blue triangle) and $R_{U\rightarrow D}$ (red inverted triangle) at 80 K converted from telegraph noise as shown in g–i. Here, the rate is measured with $V_s = -0.65$ V, and then the force curve is measured with $V_s = -0.0$ V at the same position using the same tip apex and common z. Dotted lines are included as a guide to the eye. Solid lines indicate the short-range force for the U state (red) and the D state (blue). (k), Potential energy surface as a function of the reaction coordinates is schematically drawn for z = 1.5 Å (blue), 0.5 Å (black), and 0.0 Å (red). (1) Sequential AFM image, Δf -z curve, STM image and I_t -t telegraph noise showing alternate force-induced upward switching and current-induced downward switching with a fixed lateral tip position as indicated by white and black dots.

The downward switching process $U \rightarrow D$ is more frequent because the tunneling current mainly flows through the U-sites for two reasons: (i) Si atoms of the tetramer in the UP position are relatively closer to the tip apex and (ii) the electrons tunnel through an HOMO state that is mostly localized on atoms in the up position (see Figure 2i).

The switching mechanism can be explained by a process that is similar to the desorption induced by an electronic transition (DIET) mechanism.²⁶ During a single electron tunneling process, a hole is first created in the HOMO state as an electron tunnels to the tip, and the Si₄-QD is positively charged. After a certain time, the hole recombines with an electron from the reservoir of bulk electrons, and the Si₄-QD is neutralized. During this process, the Si₄-QD alternates between two potential energy surfaces (PES): a neutral \rightarrow +1e charged \rightarrow neutral. Because the atomic configuration of the ground states of the neutral and charged PES differ, each charging or discharging event yields a change of potential energy that is converted into an increase of the kinetic energy as shown schematically in Figure 3n. Indeed our theoretical analysis based on constrained DFT simulations shows that, for each hole created, the Si4-QD may gain a kinetic energy of up to \approx 0.50 eV, as the sum of 0.22 and 0.28 eV from the movement

induced on the PES^{+1e} and PES⁰ after the charging and discharging event, respectively. This energy is enough to overcome the relevant activation barrier, $E_{\rm b} = 0.44$ eV. Thus, our results show that the stochastic one-electron switching between L and R states is feasible. For a more detailed analysis of the current-driven switching mechanism see Figure S7.

We have been able to manipulate the Si₄-QD not only with the tunneling current but also mechanically with the atomic force of a NC-AFM. Figure 4a-e shows the evolution of a constant frequency shift in NC-AFM images with decreasing tip-sample distance. The images were acquired with a zero applied bias ($V_s = 0.0 \text{ mV}$) to rule out any influence of the current-induced switching. In the far tip-sample distance, which corresponds to a frequency shift Δf of -3.7 Hz, we identify a faint diagonal formed by two bright protrusions corresponding to the L and R states of the Si₄-QD (see Figure 4a and b), similarly to STM contrast (see Figure 3b). The measured lateral distances of 3.8 Å and the height difference of \sim 0.1 Å between the two bright protrusions are consistent with an atomic configuration of the upper atoms of the Si₄-QD model obtained from the DFT calculations (Figure 2g). At shorter z-distance ($\Delta f = -3.8$ Hz), we begin to observe switching during the imaging, as indicated by the dotted line in

Figure 4c. If we approach the tip closer ($\Delta f = -3.9$ and -4.1 Hz), a square-shaped pattern ("square Si₄") becomes visible as a result of sum of the bright areas of the L and R states (schematically drawn in Figure 4f). The characteristic pattern originates from an upward movement of the Si atom, below the tip. We should note that the force-induced switching shows almost no switching noise. This reveals the deterministic one-way upward switching,¹⁵ in contrast to the stochastic current-induced downward switching.

To understand the upward force-induced switching, we have combined force-distance spectroscopy taken on top of Si₄-QD atoms with DFT calculations. Figure 4g shows the experimental and calculated short-range chemical force curves acquired with the tip initially positioned over the D state of the Si atom. As the tip approaches, the chemical force increases gradually, until a sudden jump occurs at the threshold force $F_{\rm t} \approx -0.5$ nN. We learned from the DFT simulation that this corresponds to a critical distance, at which the atom located below the tip apex jumps to contact establishing a strong covalent bond with the outermost atom of the tip. Once this critical point is crossed, the Si atom always flips from the D to the U state when the tip is retracted. This is accompanied by the rearrangement of the remaining three Si atoms in the Si₄-QD, which leads to a switch from the L to the R state or vice versa (see Movie S4). In contrast, we never observed a downward switching when the tip was located above the U state, either experimentally or theoretically. A detailed description of the processes involved in the force switching can be found in Figures S12 and S13. The force-induced switching mechanism allows the same reproducibility and degree of control previously shown by the STM. This is demonstrated on Figure 4h, where a series of mechanical switches between the L and the R states is shown.

Now that we have demonstrated the feasibility of the current and force-induced switching on the Si4-QD, the question of their possible combination naturally arises. Next, therefore, we discuss the simultaneous application of the competing electronic and mechanical switching. Figure 5a-f show a sequence of STM images acquired by gradually approaching the tip toward the surface at a constant bias voltage of 0.60 V. Far from the surface, the low tunneling current inhibits any currentinduced switching. Thus, we observe a typical STM image of the Si₄-QD frozen in the R state, as shown in Figure 5f. When we begin to gradually decrease the tip-sample distance, which simultaneously increases the tunneling current, the electronically driven downward switching is induced. This in turn gives rise to the characteristic cross Si₄ contrast, as seen on Figure 5e. We should stress that at this distance the short-range force is still negligible. However, at the onset of the short-range force, the force interaction between the tip apex and an atom of the Si₄-QD located underneath becomes significant. In this regime, the current-driven switching process is still dominant but with modified upward and downward switching rates. Thus, the STM image contrast has a fuzzy quality, as seen in Figure 5c. Finally, we cross the critical threshold force F_{t} , and now the force-induced switching mechanism entirely dominates. Hence atomic the STM contrast is converted to a square Si₄ shape, as shown in Figure 5a (see also Figure S5).

To gain more insight into the competition between the current- and force-induced switching mechanisms, we performed two sets of measurements on identical Si₄-QD with the same tip apex. First, we acquired the evolution of the $R_{D\rightarrow U}$ and $R_{U\rightarrow D}$ switching rates as a function of the tip-surface distance with the tip placed over one Si atom at a bias voltage of -0.6 V.

Immediately after this, we performed force-spectroscopic analysis over the U and D atoms of the Si₄-QD at 0 V bias to determine the short-range forces acting between the tip and atoms of the Si₄-QD. Figure 5j shows the evolution of the $R_{D\rightarrow U}$ (blue triangle) and $R_{U\rightarrow D}$ (red inverted triangle) switching rates and corresponding short-range force along the tip approach (see also Figure S6). The rates were evaluated from the telegraph noise acquired at different z-distances (three examples are shown in Figures 5g–i). In order to clarify the results of these experiments, we combined them with the DFT calculations of the evolution of the activation energy barrier E_b between the L and R states upon tip approach (see Figure Sk).

Far from the atom, where the short-range chemical force is not present, the L and R states are equivalent. Therefore, the activation barriers for the transitions between the $D \rightarrow U$ and $U \rightarrow D$ states are the same, i.e., $E_b \sim 0.4$ eV. In this situation, the switching rate is exclusively driven by the downward current-driven switching, where the rate $R_{U \rightarrow D}$ prevails. However, the situation changes upon the onset of the shortrange chemical force, where the potential energy landscape of the Si₄-QD is modified by the tip proximity. According to the DFT calculations, not only is the activation barrier changed substantially, but the U state also becomes more energetically favorable (see Figure 5k). Consequently the activation barrier becomes asymmetric with $E_b^{U \to D} > E_b^{D \to U}$, and the switching rates $R_{\mathrm{D} \rightarrow \mathrm{U}}$ and $R_{\mathrm{U} \rightarrow \mathrm{D}}$ are accordingly renormalized. This transition regime is clearly identified in Figure 5j, where the short-range force is no longer negligible and the switching rates $R_{D \rightarrow U}$ and $R_{U \rightarrow D}$ become equal. Finally, the activation barrier vanishes completely when the chemical force reaches a threshold value F_t and the upward mechanical switching prevails completely (see also Movie S5).

To demonstrate the precise control over the two different mechanisms, we sequentially switched a selected Si₄-QD between the L and R states back and forth using two competing STM and AFM switching mechanisms, as shown in Figure 5l. Namely, we performed a series of subsequent upward and downward switches with the tip placed in a fixed lateral position, as denoted by the dot in Figure 5l. First, we employed Δf -z spectroscopy with $V_s = 0.0$ V with the tip positioned over the D state (marked on Figure 5l) for the upward switch transforming the R to L state. Next, at the same position, we applied a bias pulse of -0.65 V for 1 s for the downward switch inducing the L \rightarrow R transition.

In summary, we have demonstrated controlled switching of the bistable Si₄-QD on an Si surface at 80 K by means of a tunneling current and an atomic force. To our knowledge, this represents the first simultaneous application of two competing switching mechanisms on a nanoscale object. By combining the experimental evidence with theoretical calculations, we have described in detail two competing switching mechanisms: the downward switching mechanism driven by tunneling current (STM) and the upward switching driven by the attractive shortrange force (AFM). The combination of AFM and STM allows (i) the selective upward and downward switching on the same Si-QD and (ii) tuning of the upward and downward switching rate by mixing the two competing mechanisms. We believe that the simultaneous use of the AFM and STM mechanisms represents a new and versatile method for atomic manipulation and switching processes. The concept of controllable tuning of switching rates by means of the simultaneous application of force- and current-induced mechanisms might be, in principle, extended to other systems such as molecules, nanostructures,

etc., in different environments ranging from UHV to ambient or liquid environments.

Methods. *Experimental Details.* Highly doped *n*-type (Asdoped, $\rho = 0.002 \ \Omega \ cm$) Si(111) single crystals were used as substrates. Si(111) samples were degassed in an ultrahigh vacuum ($P < 1 \times 10^{-9}$ Pa) at 650 °C for 12 h and subsequently flashed at 1200 °C for 5 s to prepare atomically clean Si(111)-7 \times 7 surface reconstruction. Then Si was evaporated on the Si(111)-7 \times 7 surface kept at RT from a Si-wafer evaporator by Joule heating of direct current. In RT-AFM/STM experiments, Si₄ was fabricated from Si₁ using atom manipulation (see Figure S1).²¹ In contrast, in the low temperature (LT) STM and AFM switching demonstration, native Si₄ was sought and examined.^{27,28}

We employed a commercial Omicron LT-AFM/STM machine operated at 80 K in an ultrahigh vacuum (UHV) ($P < 1 \times 10^{-8}$ Pa). We used qPlus sensors¹⁷ with a spring constant k = 2000 N/m. AFM was operated in the frequency modulation mode²⁹ with a typical resonant frequency of $f_0 = 24$ kHz, by keeping the oscillation amplitude at A = 10 Å. The same tip apex was used for each set of experiments. Force spectroscopic measurements were carried out using a Matrix controller. Site-specific Df-*z* curves were measured on the Si atoms as well as the corner hole sites. The long-range force contribution could be estimated by the Df-*z* curve on the corner hole site, since atoms are missing up to the third layer below the tip. After the long-range part of Df was subtracted from the Df-*z* curves on the Si atoms, they were converted into the short-range force curves using the inversion formula.³⁰

Computational Details. Theoretical DFT-based calculations were performed using the fast local orbital DFT Fireball code.²² The accuracy was tested with a plane-wave VASP code.³¹ The nudged elastic band method was used in order to reveal the reaction pathway.²⁴ The STM simulations of an Si tetramer structure were performed using Green's function formalism.²³ A more detailed description of the employed methods can be found in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

Additional information related to the atom manipulation and assembling of Si₄, simultaneously acquired AFM and STM image of Si₄, transition of switching behavior during tip approach and retraction, and detailed theoretical description of the current induced switching mechanism of the Si₄ and AFM calculations. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/ acs.nanolett.Sb00448.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Joachim, C.; Gimzewski, J. K.; Aviram, A. Electronics using hybrid-molecular and mono-molecular devices. *Nature* **2000**, *408*, 541–548.

(2) Eigler, D. M.; Lutz, C. P.; Rudge, W. E. An atomic switch realized with the scanning tunnelling microscope. *Nature (London)* **1991**, *352*, 600–603.

(3) Moresco, F.; Rieder, G.; Tang, K.-H.; Gourdon, H.; Joachim, A.; Conformational, C. Changes of Single Molecules Induced by Scanning Tunneling Microscopy Manipulation: A Route to Molecular Switching. *Phys. Rev. Lett.* **2001**, *86*, 672–675.

(4) Hata, K.; Sainoo, Y.; Shigekawa, H. Atomically Resolved Local Variation of the Barrier Height of the Flip-Flop Motion of Single Buckled Dimers of Si(100). *Phys. Rev. Lett.* **2001**, *86*, 3084–3087.

(5) Sagisaka, K.; Fujita, D.; Kido, G. Phase Manipulation between- $(c(4 \times 2))$ and $(p(2 \times 2))$ on the Si(100) surface at 4.2 K. *Phys. Rev.* Lett. **2003**, 91, 146103.

(6) Stroscio, J. A.; Celotta, R. J. Controlling the Dynamics of a Single Atom in Lateral Atom Manipulation. *Science* **2004**, *306*, 242–247.

(7) Liljeroth, P.; Repp, J.; Meyer, G. Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules. *Science* **2007**, *317*, 1203–1206.

(8) Tomatsu, K.; Nakatsuji, K.; Iimori, T.; Takagi, Y.; Kusuhara, H.; Ishii, A.; Komori, F. An Atomic Seesaw Switch Formed by Tilted Asymmetric Sn-Ge Dimers on a Ge (001) Surface. *Science* **2007**, *315*, 1696–1698.

(9) Perera, U.; Ample, F.; Kersell, H.; Zhang, Y.; Vives, G.; Echeverria, J.; Grisolia, M.; Rapenne, G.; Joachim, C.; Hla, S.-W. Controlled clockwise and anticlockwise rotational switching of a molecular motor. *Nat. Nanotechnol.* **2012**, *8*, 46–51.

(10) Auwärter, W.; Seufert, K.; Bischoff, F.; Ecija, D.; Vijayaraghavan, S.; Joshi, S.; Klappenberger, F.; Samudrala, N.; Barth, J. A surfaceanchored molecular four-level conductance switch based on single proton transfer. *Nat. Nanotechnol.* **2012**, *7*, 41–46.

(11) Schaffert, J.; Cottin, M.; Sonntag, A.; Karacuban, H.; Bobisch, C.; Lorente, N.; Gauyacq, J.-P.; Möller, R. Imaging the dynamics of individually adsorbed molecules. *Nat. Mater.* **2013**, *12*, 223–227.

(12) Kumagai, T.; Hanke, F.; Gawinkowski, S.; Sharp, J.; Kotsis, K.; Waluk, J.; Persson, M.; Grill, L. Controlling intramolecular hydrogen transfer in a porphycene molecule with single atoms or molecules located nearby. *Nat. Chem.* **2014**, *6*, 41–46.

(13) Inami, E., Hamada, I., Ueda, K., Abe, M., Morita, S., Sugimoto, Y. Room-temperature concerted switch made of a binary atom cluster *Nat. Commun.* 62015accepted.

(14) Loppacher, C.; Guggisberg, M.; Pfeiffer, O.; Meyer, E.; Bammerlin, M.; Luthi, R.; Schlittler, R.; Gimzewski, J.; Tang, H.; Joachim, C. Direct Determination of the Energy Required to Operate a Single Molecule Switch. *Phys. Rev. Lett.* **2003**, *90*, 066107.

(15) Sweetman, A.; Jarvis, S.; Danza, R.; Bamidele, J.; Gangopadhyay, S.; Shaw, G. A.; Kantorovich, L.; Moriarty, P. Toggling Bistable Atoms via Mechanical Switching of Bond Angle. *Phys. Rev. Lett.* **2011**, *106*, 136101.

(16) Pawlak, R.; Fremy, S.; Kawai, S.; Glatzel, T.; Fang, H.; Fendt, L. A.; Diederich, F.; Meyer, E. Directed Rotations of Single Porphyrin Molecules Controlled by Localized Force Spectroscopy. *ACS Nano* **2012**, *6*, 6318–6324.

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(17) Giessibl, F. J. High-speed force sensor for force microscopy and profilometry utilizing a quartz tuning fork. *Appl. Phys. Lett.* **1998**, *73*, 3956–3958.

(18) Majzik, Z.; Setvín, M.; Bettac, A.; Feltz, A.; Cháb, V.; Jelinek, P. Simultaneous Current, Force and Dissipation Measurements on the Si(111)-7 \times 7 Surface with an Optimized qPlus AFM/STM Technique. *Beilstein J. Nanotechnol.* **2012**, *3*, 249–259.

(19) Ternes, M.; Lutz, C. P.; Hirjibehedin, C. F.; Giessibl, F. J.; Heinrich, A. J. The Force Needed to Move an Atom on a Surface. *Science* **2008**, 319, 1066–1069.

(20) Loppacher, C.; Bammerlin, M.; Guggisberg, M.; Schar, S.; Bennewitz, R.; Baratoff, A.; Meyer, E.; Guntherodt, H.-J. Dynamic force microscopy of copper surfaces: Atomic resolution and distance dependence of tip-sample interaction and tunneling current. *Phys. Rev.* B **2000**, *62*, 16944.

(21) Sugimoto, Y.; Yurtsever, Y.; Hirayama, N.; Abe, M.; Morita, S. Mechanical gate control for atom-by-atom cluster assembly with scanning probe microscopy. *Nat. Commun.* **2014**, *5*, 4360.

(22) Lewis, J. P.; Jelinek, P.; Ortega, J.; Demkov, A. A.; Trabada, D. G.; Haycock, B.; Wang, H.; Adams, G.; Tomfohr, J. K.; Abad, E.; et al. Advances and Applications in the FIREBALL ab Initio Tight-binding Molecular-dynamics Formalism. *Phys. Stat. Sol. B* **2011**, *248*, 1989–2007.

(23) Blanco, J. M.; Flores, F.; Pérez, R. STM-theory: Image potential, chemistry and surface relaxation. *Prog. Surf. Sci.* 2006, *81*, 403–443.

(24) Henkelman, G.; Jónsson, H. Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points. *J. Chem. Phys.* **2000**, *113*, 9978–9985.

(25) Stipe, B. C.; Rezaei, M. A.; Ho, W. Inducing and Viewing the Rotational Motion of a Single Molecule. *Science* **1998**, 279, 1907–1909.

(26) Betz, G., Varga, P. Desorption induced by electronic transitions, DIET IV: proceedings of the fourth international workshop; Gloggnitz, Austria, October 2–4, 1990; Springer-Verlag.

(27) Tanaka, H.; Yokoyama, T.; Sumita, I. Scanning Tunneling Microscope Observation of $Si(111)7 \times 7$ Formed by Si Deposition. *Jpn. J. Appl. Phys.* **1994**, 33, 3696–3701.

(28) Sato, T.; Kitamura, S.; Iwatsuki, M. Initial adsorption process of Si atoms on an Si(111)7 \times 7 surface studied by scanning tunneling microscopy. *Surf. Sci.* **2000**, 445, 130–137.

(29) Albrecht, T. R.; Grütter, P.; Horne, D.; Rugar, D. Frequency Modulation Detection using High-Q Cantilevers for Enhanced Force Microscope Sensitivity. J. Appl. Phys. **1991**, *69*, 668–673.

(30) Sader, J. E.; Jarvis, S. P. Accurate Formulas for Interaction Force and Energy in Frequency Modulation Force Spectroscopy. *Appl. Phys. Lett.* 2004, *84*, 1801–1803.

(31) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186.