Role of tip chemical reactivity on atom manipulation process in dynamic force microscopy

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The procedure for force spectroscopy and atom manipulation with the same tip

We scanned the Si(111)-(7×7) surface by AFM, and select a surface region that is suitable for atom manipulation experiments near the center of terrace. A Si adatom vacancy was created by

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mechanical atom extraction technique.[1] The procedure for this process is outlined below: Firstly, AFM scan was stopped and the tip was brought over a Si adatom to be removed. After the feedback for the regulation of the tip-surface distance was opened, the tip approached the surface by certain displacement and retracted to the original height. Then, the feedback was reactivated and AFM scan was carried out to check the atom extraction. The controlled indentation procedure was repeated with gradual increment of the displacement until a Si adatom vacancy was successfully created. If the tip state became unstable after atom extraction, the tip was laterally moved to different surface area, typically 10 nm away from the created vacancy site, and the tip state was changed by intentional tip-surface contact or by AFM scanning under the close tip-surface distances until the tip state was stabilized. When the clear atomic resolution was obtained and the tip state was so stable that no further tip changes occurred during scanning even under close tip-surface distances, the tip was brought to the area where the vacancy was created and AFM topographic image was obtained over this region.

Prior to the lateral atom manipulation experiments, force spectroscopic measurements were carried out above a Si adatom to characterize the tip apex reactivity. The $\Delta f(z)$ curves were acquired above the adatom with lateral precision of 0.1 Å using atom tracking as described elsewhere.[2] Afterwards, atom manipulation experiments were started. To precisely adjust the scan line just above the center of the vacancy and the manipulated adatoms, the tip was firstly positioned above another Si adatom above the line but in a different half unit cell by atom tracking. After the thermal drift was compensated by the feedforward controller,[3] the atom tracking was turned off and successive line scans were carried out above the line connecting the vacancy and the manipulated Si adatoms in the $[1\bar{1}0]$ direction. The scan direction was precisely aligned parallel to the $[1\bar{1}0]$ direction by the versatile scan controller.[4]

We applied constant height scans where the tip-surface feedback was turned off to compare atom hopping probability and the interaction force at the specific height. In addition, this scanning mode is indispensable to the risk reduction of the tip crash during atom manipulation. The slope of the $\Delta f(z)$ curves above the adatom sites change the polarity at close tip-surface distances where

atom hopping probability is large because the long-range force is relatively small for sharp Si cantilevers.

Atom manipulation with the different set of tips

In Figure S1, we supply the atom hopping probability plots together with $F_z(z)$ and $U(z)$ curves obtained with different tip state and cantilever from those used in Figures 2A, 2B and 2C of the original manuscript. We found that the Si adatoms cannot be moved from the Co to M sites in either forward and backward scan directions even at distances where F_z on Si adatom reaches the repulsive force region. These results clearly show the importance of tip states in atom manipulation process in dynamic AFM.

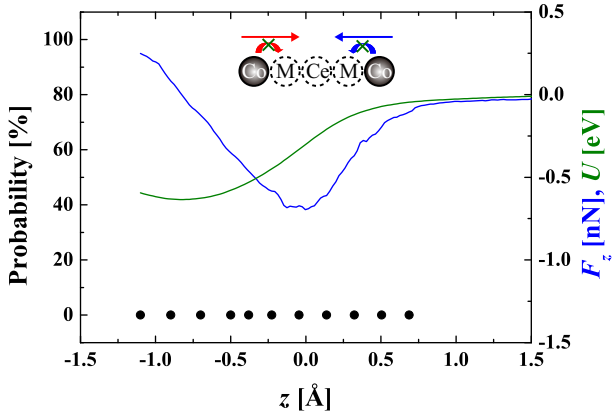

Figure S1: The atom hopping probability plots together with $F_z(z)$ and $U(z)$ curves above the Si adatoms obtained with a different cantilever from those used in Figures 2A, 2B, and 2C of the original manuscript.

The dependence of the manipulation probability on adsorption site

Although we did not mention in the main text to focus on the main messages of the work, we can also investigate the dependence of the manipulation probability on the adsorption sites. By

comparing the distance dependence of the measured probability curves (see Figures 2A and 2C of the original manuscript), it is revealed that the relative probability for adatom hopping from Ce to the M site (black triangles) is higher than that from Co to the M site (blue circles) at the same tip-surface distances and identical scan direction, which reflects the difference in the diffusion energy barrier. Indeed, previous experimental investigations based on adatom extraction[5] and displacement[6]–acquired by applying a voltage pulse to the Si(111)-(7×7) surface–have supported our investigations, suggesting a higher energy barrier associated with the transition from the Co to the M site.

Dissipation and amplitude

Figures S2 show the distance dependence of the energy dissipation and the oscillation amplitude of the cantilevers, which were simultaneously obtained with Δf curves during force spectroscopic measurements. (A), (B), (C), and (D) correspond to $F_z(z)$ curves in Figure 2A, Figure 2B, Figure 2C, and Figure S1, respectively. We do not observe any significant changes in the dissipation channel even at close tip-surface distances within the experimental error. This suggests that the tip apex is so stable that there are no tip structural changes and instabilities under the high load at small tip-sample separations.

In addition to this information, we should note that the dissipation during the atom manipulation process was also measured at constant height scans (not shown here). The results of these measurements do not provide any significant dissipation signal that is visible within our experimental error. The invisibility or the small value of the dissipation signal during the manipulation process can be attributed to mainly two different sources. The first one is the temperature effect. The atomic jumps during the manipulation process may result in increase in atomic scale dissipation. However, the expected sharp changes in dissipation signal has strong temperature dependence,[7] and it can be smoothed out with higher temperatures. Another effect which could also play a role in the observed vanishing of dissipation signal during atom manipulation process is the

fact that the atomic jumps are not occurred in every tip oscillation cycles, but just in single or a few tip oscillations.

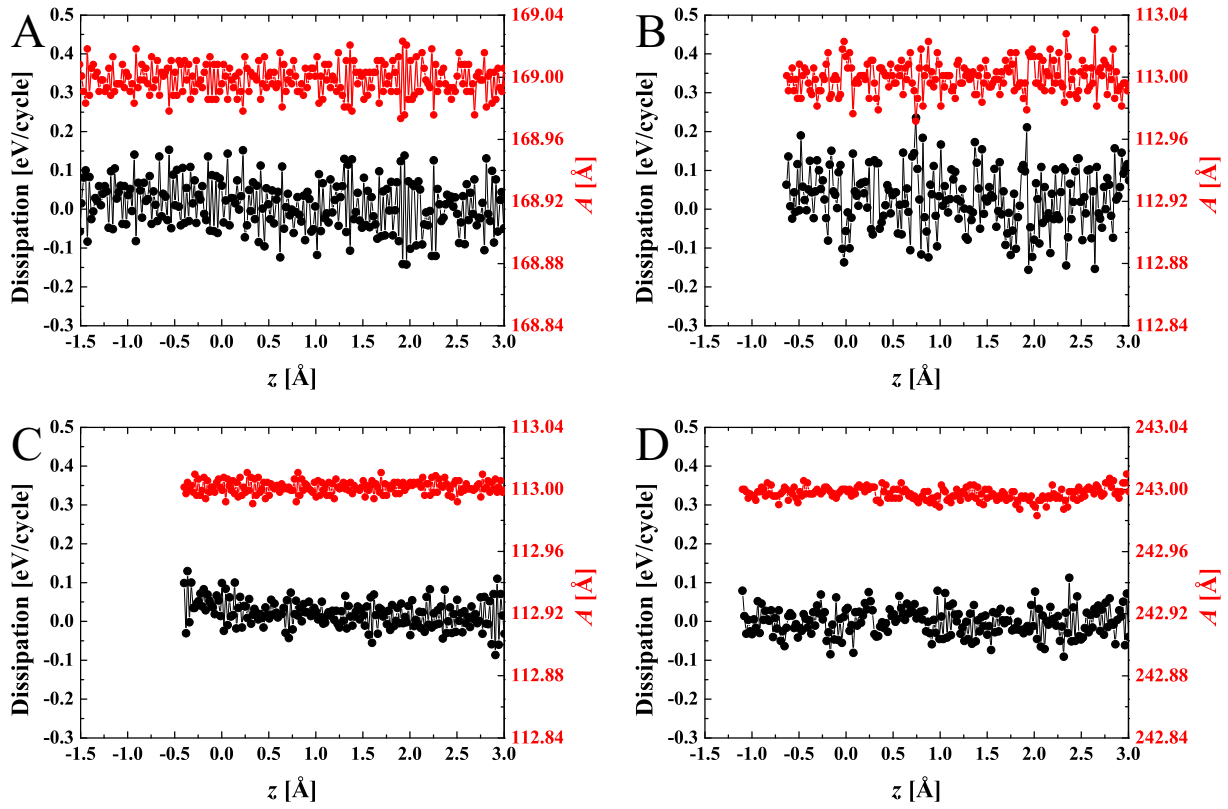

Figure S2: The distance dependences of the energy dissipation and the oscillation amplitude of the cantilevers. (A), (B), (C), and (D) correspond to Figure 2A, Figure 2B, Figure 2C, and Fig. S1, respectively.

Acquisition Parameters

Data	f_0 [Hz]	k [N/m]	A [Å]	V_s [mV]	Q
Fig. 1 and Fig.2A	156 700.2	26.5	169	-134	13 000
Fig.2B and Fig.2C	156 925.3	26.7	113	-306	12 000
Fig. S1	156 707.4	26.5	243	-161	13 000

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