Detailed Single Atom Manipulation Mechanisms during a Quantum Corral Construction

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We describe a complete picture of how single Ag atoms move on the various potential energy landscapes of a Ag(111) surface during a quantum corral construction by using a scanning tunneling microscope (STM) tip at 6 K. The threshold tunneling resistance and tip-height to move the Ag atom across the surface are experimentally measured as $210 \pm 19 \text{ k}\Omega$ and $1.3 \pm 0.2 \text{ Å}$. The experimental atom manipulation signals reveal remarkably detailed atom movement behaviors dependent on the surface crystallographic orientation and offer atomic-level tribology information.

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‘Bottom up’ approach is one of the main focus research areas of nanoscience [1,2] where various atomic structures will be constructed on an atom-by-atom basis. Manipulation with a STM-tip allows engineering of man-designed structures using single atoms/molecules or investigating the physical/chemical properties of materials at an atomic level [1-11]. Positioning of single atoms with sub-atomic level precision on a surface requires an extremely fine control over the tip-atom-surface junction. The detailed knowledge of how an atom moves across a surface is valuable for both fundamental understanding and further progress of nanoscience.

The experiments were conducted by using a low temperature UHV-STM operated at ∼6 K. The Ag(111) surface was cleaned by repeated sputter-anneal cycles [7]. An etched W wire was used as the STM-tip. Single Ag atoms for the experiment are produced in-situ by manipulating the native substrate with the tip. The detailed tip preparation and in-situ single atom production procedures will be published elsewhere. To construct the quantum corral, Ag atoms are relocated on the surface using the ‘lateral manipulation’ procedure [2,12-14]. It involves approaching the tip toward the atom and then moving the tip along a chosen path in a constant current mode. At the final destination, the tip is retracted back to the initial imaging height leaving the atom at the desired location on the surface.

To investigate the tip-atom interaction responsible for the manipulation process, the tunneling resistance necessary to move the atom was first determined. We have developed a computer controlled automated-manipulation scheme for this purpose. Initially, the computer automatically located the position of a single atom and then the atom is moved across the surface to a random final location selected by the computer. For each bias, the atom was manipulated by using different current values (from 8 to 950 nA). For each set of
current and bias, 24 or more manipulations were done. Fig. 1a shows the manipulation probability vs. tunneling current plot at -45 mV. In this bias, the probability changes from 0 below 147 nA to 1 above 250 nA. The average threshold current is determined as 200 nA.

By changing the bias, the entire procedure is repeated. An extensive set of 3857 computer-automated measurements has been taken for the bias range from ±10 to ±55 mV. Evaluation of these data yields the minimum current necessary to move the atom as a function of the bias averaged over all surface directions. Fig. 1b depicts the results, which clearly display a linear dependence between the tunneling voltage and the threshold current, independent of the bias polarity. Each data point here is determined by plotting a curve like in Fig. 1a. From the slope of the curve, a tunneling resistance ($R_t$) of $210 \pm 19 \, \text{k}\Omega$ has been measured (Fig. 1b). This linear relationship indicates that the ‘$R_t$’ is the ultimate matter to move an atom within the bias range used. The tip-surface distance is calibrated by measuring ‘$R_t$’ as a function of tip-height (Fig. 1c). This is accomplished by acquiring the I-Z spectroscopy. The calibration reveals that the $R_t$ of 210 kΩ corresponds to a distance of $1.3 \pm 0.2$ Å (Fig. 1c). Due to this close distance, we estimate that chemical nature of tip-atom interaction is the main driving force in our manipulation process.

During the circular quantum corral (Fig. 2) construction, the tip speed is fixed to 10 Å/s. We use $R_t = 15 \, \text{k}\Omega$, which is well below the measured threshold value. At this distance, the tip is in almost mechanical contact with the atom. The manipulation paths are precisely determined on the basis of atomic resolution STM images of the surface. Because the thermal drift of our STM is less than 1 Å/hr at 6 K, we are able to manipulate atoms back and forth on the same manipulation path for many times. To ensure reproducibility we repeat the manipulation at least 10 times for each path, totaling over 360 manipulations for
the corral construction alone. In addition, atom manipulations are also performed at separate locations to verify the specific features observed in the manipulation signals.

Initially, each atom was positioned at the center of the corral (Fig. 2a and 2c) and then relocated to a final position. The manipulation path of the first atom was chosen along a surface atomic close-packed (CP) row (Fig. 2c), i.e. along [110]. Then, next atoms were moved along a direction 10° rotated from the previous paths (Fig. 2c and 2d). Thus, a total of 36 atoms are required for 360° to complete a circle. For simplicity, we will discuss the various tip-paths as a function of deviation angle ‘θ’ from the CP rows (Fig. 2d). On an fcc(111) surface, CP rows are located at every 60° (Fig. 2d). In addition, because of the surface mirror symmetry, the tip-paths for θ = 10° and 50° and for θ = 20° and 40° encounter the same surface geometry (Fig. 2d). Thus, analyses on the atom movements between θ = 0° and 30° tip-paths are sufficient to cover all surface directions.

The atom moves in the ‘pulling mode’ [13,14] along the CP rows (θ = 0°) indicating the attractive tip-atom interaction [12]. The 2.89 Å hop-length (Fig. 3) shows that it visits only one kind of site, either hcp or fcc, upon following the tip. Due to a lower diffusion barrier, the CP rows are the most favored atom traveling paths [12,16]. Complex manipulation signals are observed when the paths deviate from the CP rows. Fig. 3 collects experimental atom manipulation signals along various tip-paths.

In 10° tip-path, the manipulation signals include smaller steps (Fig. 3) caused by the atom visiting of both fcc and hcp sites (Fig. 4). This is induced due to a slight lateral displacement of the tip-apex to the left or right side of the CP row where the atom is traveling (Fig. 4), but the tip is still in a close-proximity of the atom [12]. As the tip continues to move along its 10° path, the atom follows the tip by traveling along the CP row.
Due to different directions, the tip-atom distance increases and the tip-atom interaction reduces. Finally, the atom is traveling by visiting only single sites, either fcc or hcp, again (larger steps). Continuation of the tip movement along $10^\circ$ path leads to increase the tip-atom distance further. Since now the atom is no longer directly located under the tip-apex, the tip moves closer to the surface. This increases the lateral force component, $F_x$ (Fig. 4). When $F_x$ is large enough to overcome the surface potential barrier, the atom hops to the next CP row to follow the tip. Now it is in a close proximity with the tip-apex again. From that point another series of single and hcp-fcc sites traveling sequence is repeated.

A different kind of manipulation signal is observed when manipulated along the $\theta=20^\circ$ tip-path (Fig. 3). The distinctive features in this signal are the periodic deep-slopes. The specific atom movement can be perceived as follows: When ‘$\theta$’ becomes larger, the intersection time between the tip-path and the adjacent surface CP rows becomes shorter. Yet, the atom still prefers to travel along the CP row and in doing so it moves away from the tip shortly after such an intersection (Fig. 4). At one point it can no longer continue to move along the CP row because of the large tip-atom distance. Then the atom stops traveling and rest for some time, as if it confuses what to do next (Fig. 4). This behavior can be regarded as a competition between the atom’s preferential traveling along the CP row and its duty to follow the tip. The tip continues its scan by following the down-slope of the now resting atom’s edge that results in falling of the tip-height to a lower value (Fig. 3) and thereby increasing the lateral force, $F_x$. When $F_x$ overcomes the hopping barrier, the atom jumps back under the tip which is now already above the next CP row. This hopping alerts the STM feedback system to retract the tip resulting in a rapid increase of the tip-height signal (Fig. 3 and Fig. 4). The atom travels by repeating this ‘move-rest-jump’ cycle [17].
When $\theta = 30^\circ$, the tip-path no longer intersects with the CP rows (Fig. 2b). Thus, the atom cannot follow the tip by traveling along a CP row. The surface geometry along this path includes repeating units of three hollow sites. The first two sites, ‘a’ and ‘b’, are 1.67 Å apart and the third site ‘c’ is 3.33 Å apart from ‘b’ (Fig. 4 and Fig. 2b). The atom moves in a ‘sliding mode’ [13,14] between ‘a’ and ‘b’ producing two smooth bumps with 1.7 Å apart in the signal (Fig 3 and Fig. 4). It does not travel directly from ‘b’ to ‘c’ due to a higher hopping barrier caused by a relatively far distance between these two sites. The theory predicts the nearest and the next nearest local minimum energy locations for the atom as the two adjacent hollow sites, ‘d’ and ‘e’ (Fig. 4) [12]. The manipulation signal shows that after moving the down-slope of the atom contour at site ‘b’, the tip starts to climb up the new atom contour which belongs to the site ‘c’ (Fig. 3, Fig. 4). This indicates that the atom has already moved in front of the tip. Instead of moving straightforward along the tip-path, the atom finds its way to the site ‘c’ by smoothly sliding through the two nearby sites ‘d’ and ‘e’ resulting in an approximately semi-circle traveling path (Fig. 4) [17]. In this way it avoids entering under the tip-apex and thus, no apparent signature can be observed in the manipulation signal. To further support these atom movement behaviors, we have manipulated Ag atoms along $\theta = 5^\circ$, 15$^\circ$ and 25$^\circ$ tip-paths, half ways between the angles we discuss above. At $\theta = 5^\circ$, the tip remains in a close proximity of the CP row for a longer time than at $\theta = 10^\circ$. As a result, the number of smaller steps (hcp-fcc hopping) is increased in this path. The manipulation signal for $\theta = 15^\circ$ [17] shows similar structure as for $\theta = 20^\circ$ with a reduced frequency of deeper-slopes. At $\theta = 25^\circ$, the manipulation signals consist of mixed features from the 20$^\circ$ and 30$^\circ$ paths. Even though we used a fixed tip-sample distance and the same tip speed for all the atom manipulations described above, the
atom movement styles are completely different and dependent on the surface potential energy landscapes. A sudden transition from a pronounced discontinuous movement at $\theta = 20^\circ$ path to a smooth sliding movement at $\theta = 30^\circ$ path occurs [17]. This shows that at the atomic scale the surface potential energy configuration plays a key role in tribology aspects.

In summary, our experimental report yields intimate details of atom movement mechanisms as well as atomic level tip-atom interaction during STM manipulations and provides an important step forward for the progress of bottom-up approach in nanoscience. This project was partly funded by DFG RI 472/3-2, SFB 290/TPA5 (KFB, KHR) and United States Department of Energy, BES, DE-FG02-02ER46012 (SWH) grants.

References:


[17] See EPAPS Document No. EPRBMDO-67-R18316 for animation movies of the atom movement mechanisms. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.

**Figure Captions**

FIG. 1. Tunneling resistance ($R_t$) for a successful atom manipulation. (a) The probability to move an Ag atom vs. tunneling current at -45 mV. (b) The measured threshold current, accumulated from 3857 automated atom-manipulations, reveals its linear dependence on the tunneling voltage. (c) The $R_t$ vs. tip-height on a Ag(111) surface at 46 mV bias. The ohmic-contact (tip-surface contact) point is indicated with an arrow. Dashed lines are drawn to guide the threshold $R_t$ to move an atom and the corresponding tip-height.

FIG. 2 (Color). Quantum corral construction. 3-D STM images show (a) during construction and (b) after completion of the corral. 36 Ag atoms (white protrusions) are
used (diameter = 31.2 nm). An STM image (c) and a sphere model (d) demonstrate the tip-paths and the surface geometry encountered during manipulations.

FIG. 3. Single atom manipulation signals. \( \theta = 0^\circ \) signal shows ‘pulling mode’ with the single site atom hops (2.89 Å). At \( \theta = 5^\circ \), small steps at the middle part is due to fcc-hcp site visiting of the atom. In \( \theta = 10^\circ \) signal, two series of small steps are separated by large steps in between. At \( \theta = 15^\circ \), the periodic appearance of the deep down-slopes followed by a rapid tip-height increase is due to the ‘resting’ and then ‘jumping’ of atom to the next CP row. The ‘rest-jump’ circle frequency increases at \( \theta = 20^\circ \). The \( \theta = 30^\circ \) signal includes two consecutive bumps (1.7 Å apart) followed by the next pair with 3.3 Å. At \( \theta = 25^\circ \), the manipulation signal reveals both structures of \( \theta = 20^\circ \) and \( 30^\circ \).

FIG. 4 (Color). Detailed atom movement mechanisms. The atom movements along various tip-paths are demonstrated by super exposing an actual 3-D STM image of the Ag(111) with the manipulation signals. The atom briefly rests at the square locations in \( 20^\circ \) path. When lateral force component \( F_x \) (lower right drawings) exceeds the hopping barrier, the atom jumps to the adjacent CP row (shown by red arrows) to follow the tip. At \( 30^\circ \) path, the atom slides the first two sites ‘a’ and ‘b’ producing two consecutive bumps in manipulation signals (Fig. 3). It then travels through the sites, ‘d’ and ‘e’ to reach the site ‘c’. The two drawings at the lower right corner demonstrate that the magnitude of \( F_x \) is dependent on the tip positions.
Figure 1
Figure 3
Figure 4