Atomic hop-scotch: different manipulation modes of single Cu atoms on Cu(111)

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Abstract

Single Cu atoms manipulated with a STM-tip at low temperatures across a Cu(111) surface reveal movement patterns which closely resemble classical movement of e.g. ping-pong balls on a muffin tin. Being pulled by the tip, they hop from one adsite to the next in a variety of patterns, whereby they can even occupy intermediate sites off the direct line of their movement, if the tip-atom force is chosen in the appropriate range. © 1998 Elsevier Science B.V.

With the advent of quantum mechanics and its application to matter it became apparent that classical mechanics provides in many cases a grossly inadequate approach to effects on the atomic scale. Indeed, as Binnig and Rohrer started to work on the scanning tunneling microscope (STM) many people believed that their aim of reaching atomic resolution was impossible. However, only eight years after Binnig and Rohrer's success in 1982 [1] to prove atomic resolution in surface imaging, Eigler and Schweizer [2] went an important step further by proving that the STM is not only able to image but also to manipulate atoms.

A detailed understanding of the processes involved in the manipulation procedure is indispensable for developing the technique into a (highly desired) reliable engineering tool on atomic scale. Experiments in this direction have become possible only very recently [3]. On a stepped Cu(211) surface we were able to distinguish between discontinuous (pulling) and continuous (sliding) manipulation employing attractive interactions between tip and manipulated metal atoms on the one hand and discontinuous manipulation of CO-molecules via repulsive tip-molecule interactions (pushing) on the other hand. Here we demonstrate, that on the flat Cu(111)-surface upon manipulation of Cu-atoms in the pulling mode even finer details can be resolved: Depending on the force between tip and atom (as measured by the tunneling resistivity) and the exact position of the tip apex relative to the atom, jumps may be induced in which both hcp and fcc adsites are visited and the atom follows the tip in a zig-zag path or – with smaller force – only one type of adsites is visited and the particle follows the tip in a more straight manner. Thus, the forced motion of a Cu-atom across a flat Cu(111)-substrate bears strong resemblance to the classical example of a ping-pong ball rolling on a flat muffin tin, whereby the holes represent the adsites on the surface.

A Cu(111) surface consists of a hexagonal pattern of atoms (Fig. 1a) with an interatomic distance of 2.55 Å. Close-packed rows of atoms correspond to the [110] direction of the surface. Due to the three-
Fig. 1. (a) Sphere model of the Cu(111) surface: The unit cell and the crystallographic directions are indicated. Atoms are shaded the darker the deeper they lie. Fcc adsites are indicated with white hexagons. (b) The arrows indicate the three possible ways of translating a Cu atom along a close packed substrate row: continuous (dotted arrow), hopping from fcc site to fcc site (dashed arrows) and hopping alternatingly to hcp and fcc sites (solid arrows). (c) The arrows indicate some of the possible ways of translating a Cu atom perpendicular to the close packed substrate rows.

fold symmetry of the surface, there is every 120° an analogue kind of direction. Close-packed rows occur every 60°. Two different threefold coordinated adsites exist on Cu(111): hcp-sites with an atom directly under them in the second layer of the substrate and fcc-sites with an atom right under them in the third layer. Since copper is a fcc-metal, in bulk only the fcc-sites are occupied. As the mobility of Cu-adatoms during sample preparation is sufficiently high for Cu-atoms to reach the energetically most favorable sites, for the following we may assume, that initially all Cu-adatoms occupy fcc-sites. We note, however, that the binding energies for both kinds of sites differ only slightly.

For our experiments we used a self-built STM [4] operating between 15 K and 300 K. The present experiments were conducted at 15 K. Our Cu(111) surface was prepared by several cycles of sputtering with Ne+ and annealing to ≈ 700 K. Single atoms for the manipulation experiment were extracted from the surface with the STM tip[1]. Manipulation is performed by positioning the tip right above an atom, decreasing the tunneling gap to ≈ 4 Å by using a gap resistance approximately two orders of magnitude lower than the usual ≈ 50 MΩ at a bias of ≈ 10–100 mV and laterally translating the tip with the feedback loop on. During this translation of the tip the Cu-atom is pulled across the surface[3]. Simultaneously the tip height necessary to maintain constant current is recorded. Usual pulling velocities amount to 10–100 Å/s.

Fig. 2 shows STM-images before and after translating a Cu atom by a distance of ≈ 28 Å along a close packed row at 310 kΩ gap resistance. Additionally, the edge of a small adisland and a few CO molecules adsorbed on the surface as markers can be seen[2]. Fig. 3a shows a part of the tip height curve recorded during such a manipulation process.

Basically, there are three possible ways how the manipulation process in a direction parallel to the close-packed row could proceed using an attractive force between the tip apex and the Cu atom [3]: the atom could be drawn continuously across the surface (dotted arrow in Fig. 1b). It could hop from one fcc-adsite to the next trailing the tip (dashed arrows in Fig. 1b) and it could hop alternatingly on fcc-sites and hcp-sites (solid arrows in Fig. 1b) following the STM-tip in a zig-zag manner just in the way children play hop-scotch. As the corrugation of the substrate

[1] Electrochemically etched tungsten tips were used. However, we expect them to be covered with copper due to occasional tip-substrate contact during initial in-situ tip preparation. While manipulation is possible with most of the tips, which are sharp enough to address a single atom, reproducible tip height curves during manipulation can only be acquired with tips exhibiting metallic and low-noise imaging properties.

[2] As the CO molecules are not moved by interaction with the manipulated Cu atom passing by, they obviously do not interfere strongly with each other: the tip height curve while moving a Cu atom by a CO molecule at 10 Å distance (center to center) looks similar to a curve obtained far away from the nearest CO molecule.
Fig. 2. STM-image before and after translating a single Cu-atom along a close packed row of the substrate. Additionally the edge of an adisland and a few CO molecules adsorbed as markers can be seen. Bias: 2V, Current 1nA, Size: 50 Å × 50 Å.

is extremely small, in the first case virtually no change of the tip height during the manipulation process should be observed. However, in the second and third case sudden changes of the tip height are expected whenever the tip has travelled far enough down the slope of the Cu-atom to induce one of its hops. That is exactly what can be seen in Fig. 3a. Initially the tip travels down the slope of the atom until the lateral offset becomes so large that the in-plane component of the force between the tip apex and the Cu atom is strong enough to make the Cu-atom perform a hop following the tip. Due to this hop the tip apex is again closer to the center of the Cu-atom and thus the tip has to retract in order to maintain constant current. As a hop occurs at every ≈ 1.3 Å travelled by the tip, it is apparent that the manipulated atom moves in the hop-scotch fashion across the surface. However, if a higher gap resistance of ≈ 750 kΩ is used, which implies that the distance between the tip apex and the Cu atom is larger and the in-plane component of the attractive tip-atom force rises slower with lateral offset the Cu atom does not hop before the tip has travelled so far down its slope, that by then the most favoured destination site is the fcc-adisite 2.55 Å away from its initial site. Thus, hopping according to the dotted line in Fig. 1b is induced.

Short hops with similar separation to that shown in Fig. 3a can only be observed if the tip apex is moved along [110] right in the middle between the fcc- and hep-sites. If the tip is moved closer to one of the sites, the manipulated atom will dwell longer in that site and shorter in the other. An example for this behavior can be seen in Fig. 3c. It is easily understood why the atom stays for shorter periods at sites with a larger offset from the tip path, as this offset increases the lateral distance between the tip apex and the atom, which in turn leads to a stronger lateral component of the interaction force.

In conclusion, we have shown that the pulling of a single Cu atom across a flat surface resembles strongly a classical behaviour: the Cu atom stays at one site until the lateral force between the atom and the tip apex has become large enough to perform a hop to the next site. If there are additional sites on the surface, the atom can occupy them on its way following the tip even when they have an offset with
respect to the manipulation direction; just like ping-pong balls rolling over differently inclined muffin tins. The recognition that such fine details during the manipulation process as the ones described here can be detected, is an important step forward towards the goal of reliably building artificial entities on nanoscale, whose different structures could give rise to important differences in physical and chemical properties. For example, as we have shown that manipulation can be tuned such that both fcc and hcp adsites are visited during the process, we may expect that the particles can also be deposited at will at each kind of sites; thus, the deliberate build-up of hexagonal nanocrystals of Cu (and other fcc metals) in an atom by atom fashion appears to be within reach.

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References