Atom manipulation with the STM: nanostructuring, tip functionalization, and femtochemistry

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Abstract

We briefly survey our recent studies on the soft lateral manipulation of atoms and small molecules with the scanning tunneling microscope (STM), whereby mainly the tip–surface forces are employed. Repulsive (pushing) as well as discontinuous (pulling) and continuous (sliding) attractive manipulation modes could be distinguished on Cu(2 1 1) for CO molecules and metal atoms, respectively. In the case of pulling of Cu atoms on Cu(1 1 1) even finer details could be discerned: the adparticle may show various movement patterns visiting different surface sites upon applying different tip forces. Lateral manipulation also allows modifications of the Cu(2 1 1) substrate itself in an atom-by-atom manner by releasing atoms from six-fold coordinated kink sites and even seven-fold coordinated regular step sites. Furthermore, investigations concerning controlled vertical manipulation with emphasis on picking up single CO molecules are reported. The mechanism behind vertical transfer of CO molecules relates to ultrafast chemical processes. Vertical manipulation implies besides extending the possibilities for the build-up of nanostructures the important possibility of creating structurally and compositionally well defined tips, which may eventually lead to chemical sensitivity with the STM. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

One future possibility to build-up new devices and eventually create new material combinations consists of the atom-by-atom assembling of functional structures on solid substrates. The instrument with which manipulations on atomic scale was proven to be possible is the scanning tunneling microscope (STM) [1,2]. The two basic modes of the transport of atoms or molecules to form proper patterns consist of moving the particles along the surface whereby they maintain contact to the substrate (lateral manipulation) or picking them up with the tip and releasing them back to the surface at the desired places (vertical manipulation). For a secure control of both transfer modes, which are illustrated schematically in Figs. 1(a) and (b), the basic physical steps involved in each of the two manipulation modes have to be known.

Two research groups have up to now demonstrated reliable lateral manipulation and build-up of extended nanostructures on an atomic basis with adsorbed atoms and small molecules [1,2]. The Berlin group [3] has also proven the ability to release native substrate atoms from their highly
coordinated sites and to use them for extended nanostructuring. Until recently, however, very little was known about the basic steps by which atoms and molecules are moved on crystalline surfaces. Calculations of Buldum and Ciraci [4] and Bouju et al. [5] indicated that single Xe atoms can be pulled and pushed across a surface leading to specific conductance or tip height curves during the manipulation experiment in constant height/current mode, respectively. Experiments and calculations of Jung et al. [6] showed that upon manipulation of large molecules, internal degrees of freedom can also be excited. However, to understand these phenomena thoroughly, experiments on much simpler systems like small molecules and atoms are needed. Therefore, we discuss here the basic steps of lateral manipulation of single atoms on Cu(2 1 1) and – in detail – on (1 1 1) substrates.

In the following we discuss further details of the pulling procedure observed with Cu atoms on Cu(1 1 1). Single Cu atoms for our lateral manipulation experiments on Cu(1 1 1) were extracted from kink sites of the surface with the STM tip using the method outlined in [3]. We used electrochemically etched tungsten tips; we expect, however, that they are copper-covered due to occasional tip–substrate contacts during initial in situ tip preparation. While manipulation is possible with most tips, which are sharp enough to address a single atom, reproducible tip height curves during manipulation can – at least on Cu(1 1 1) – only be acquired with tips exhibiting metallic and low-noise imaging properties. The manipulation procedure is performed as follows: once a specific adatom is chosen to be manipulated along a given line, the tip is moved to its starting point at imaging tunneling parameters of 10–100 mV and 1–2 nA. Then the tip is scanned along the predetermined manipulation line using the same parameters in order to record the initial setup with high precision. After the tip has returned to the starting point, the gap distance is reduced to ≈4 Å by increasing the setpoint current by approximately two orders of magnitude of a bias of about

Fig. 1. Idealized sketches of: (a) the pulling procedure in lateral manipulation of single atoms on Cu(2 1 1); and (b) the picking-up and putting-down procedures of CO molecules on Cu(1 1 1). Notice that the CO stands upright on the surface and has to switch its orientation when being transferred to the tip.
10–100 mV. Thus, a gap resistance of 0.1–1 MΩ is used in the manipulation mode as compared to ≈50 MΩ in the imaging mode. Then the tip is moved laterally along the manipulation line with the feedback loop on, whereby the Cu atom is pulled across the surface. Simultaneously, the tip height necessary to maintain constant current is recorded. Finally, the tip is moved back to its starting point employing the imaging parameters to record the final setup.

Figs. 3(a) and (b) display STM images before and after moving a Cu atom along a close-packed row on Cu(1 1 1) at 310 kΩ gap resistance. The edge of a small adisland and a few CO molecules adsorbed on the surface visible in Figs. 3(a) and (b) can be used as markers. As the CO molecules are not moved by interaction with the manipulated Cu atoms passing by, the two species obviously do not interfere strongly with each other: tip height curves during moving a Cu atom by CO molecules at 10 Å distance (center-to-center) look similar to curves obtained far away from the nearest CO molecule. Fig. 3(c) shows tip height curves recorded during such manipulation processes.

In principle, there are three possible ways how the manipulation along a close-packed row on Cu(1 1 1) could proceed using an attractive force between the tip apex and the Cu atom [20]. The atom could be drawn continuously across the surface (dotted arrow in Fig. 2(b)), it could hop from one fcc-adsite to the next when following the STM tip (dashed arrows in Fig. 2(b)) or it could hop alternatingly on fcc-sites and hcp-sites (solid arrows in Fig. 2(b)), the latter mode being reminiscent of the manner children play hop-scotch. As the corrugation of the (1 1 1) substrate 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 cases 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. This is exactly what can be seen in the upper part of Fig. 3(c): initially, the tip travels down the slope of the atom until the lateral offset becomes sufficiently large, so 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 to follow the tip. Owing to this hop, the tip apex is again closer to the center of the Cu atom and thus has to retract from the surface in order to maintain constant current. As a hop occurs at every 1.3 Å traveled by the tip, it is apparent that the manipulated atom moves across the surface in the hop-scotch fashion described above (solid arrows in Fig. 2(b)). This kind of behaviour was observed with a tunneling resistance of ≈310 kΩ. 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 traveled far enough down its slope that by then, the most favored destination site is the fcc-adsite 2.55 Å away from its initial position (lower part of Fig. 3(c)). Thus, hopping according to the dotted line in Fig. 2(b) is induced.
With respect to vertical manipulation [2,7,8], in previous studies a number of different atoms and molecules have been transferred between tip and sample with the STM including single xenon [7] and silicon atoms [8,9] as well as gold clusters [10]. In other studies, adsorbate-covered tips were prepared by applying the adsorbate to the tip shaft and have it migrate to the apex [11,12], by dipping the tip into the adsorbate before starting to perform imaging [13] or by spontaneous uncontrolled picking-up of residual adsorbates [14]. Here we report on extending the method of controlled vertical manipulation reported previously for Xe atoms [2,7] to CO molecules on Cu(1 1 1). We describe a reliable way to transfer CO molecules from a Cu(1 1 1) surface to the STM tip and back to the surface. This ability adds a new, important feature to the list of STM applications, namely chemical sensitive imaging: with a tip having a CO molecule at its apex, we prove to achieve chemical contrast between otherwise similar appearing adsorbates.

Chemical resolution is of great interest in order to distinguish different chemical species via STM images. As Tersoff and Hamann [15] have shown, the profile of an STM picture is a contour of constant local density of states in the vicinity of the Fermi-edge. Small adsorbates are visible in STM images by the perturbation of the local density of states of the substrate they cause. This depends in a non-trivial way on their electronic structure and it requires considerable theoretical work to actually predict STM images of different adsorbates [16]. Comparing measured data to theoretical predictions is therefore up to now only possible for a rather restricted number of adsorbate/surface combinations.

2. Experimental

In our experiments we used a self-built STM [17] capable of operation between 15 and 300 K. All measurements described here were performed
between 15 and 50 K. The Cu(111) crystal was prepared by several cycles of sputtering with Ne ions and annealing to about 700 K. Very low coverages of CO were prepared by dosing CO molecules through a very fine hole to the sample located in the STM at 15 K.

The manipulation experiments referred to here were performed on the (111) and (211) surfaces of Cu (Figs. 2(a) and 1(a)). On Cu(111) there are two principal directions: along the close-packed rows are the [101], and perpendicular to the rows the [112] directions. Close-packed rows are found every 60°. Two different three-fold coordinated adsites exist for Cu adatoms on this surface: hcp-sites with an atom directly below these sites in the second layer of the substrate and fcc-sites with an atom below them in the third layer. In the bulk, only the fcc-sites are occupied. CO molecules adsorb on top of the substrate Cu atoms [18]. The Cu(211) surface consists of (111) nanofacets and (100) regular steps (see Fig. 1(a)); here the CO molecules adsorb at the upper step edges [19].

3. Lateral manipulation of native Cu atoms on Cu(111)

In previous work on the stepped Cu(211) surface (see Fig. 1(a)), we have shown to be able to extract native substrate atoms from six-fold coordinated kink and even seven-fold coordinated step edge-sites and to perform with these new techniques, a variety of surface structuring procedures in an atom-by-atom manner [3]. Further studies with Cu atoms and adsorbed Pb atoms and CO molecules on Cu(211) enabled us to distinguish different manipulation modes in dependence of the tip–adparticle force (as measured in a qualitative manner by the tunneling resistance): Cu and Pb atoms could be manipulated via attractive tip–particle interactions in a way, in which they follow the tip discontinuously by hopping from one adsite to the next (pulling). Upon application of larger forces (corresponding to smaller tunneling resistances) than for pulling, Pb atoms could also be manipulated attractively in a continuous mode (sliding). Finally, single CO molecules as well as rows of several CO molecules were found to be manipulated reliably via a repulsive interaction (pushing), whereby the intrinsic step edges, to which the CO molecules are bound, act as railway trails [20].

4. Vertical manipulation of CO molecules on Cu(111)

In the following, we describe a reliable procedure we developed for transferring single CO molecules from a flat Cu(111) surface to the apex of an STM tip and vice versa. A schematic picture of the basic processes involved upon transfer from the substrate to the tip is shown in Fig. 1(b). It is well known that CO is adsorbed in on-top sites and stands upright on this surface [18] with the C bonding to the metal atoms. As the CO molecules have a similar adsorption geometry on isolated Cu atoms adsorbed on Cu substrates [21], we may safely assume that the CO molecules have to flip around when being transferred vertically. Obviously, the extended number of degrees of freedom associated even with a diatomic molecule makes the situation more complicated than in the case of Xe [2,7].

We start an experiment of vertical manipulation by positioning the tip on top of a CO molecule using a sample bias of +2 V with a typical current of 1 nA. We then turn off the feedback loop, that is used to maintain a constant tunneling current, and increase the sample voltage to +3 V. Subsequently the voltage is slowly decreased to 0 V, while simultaneously decreasing the gap distance by 0.1 nm to compensate the decrease in the current. During this process, the current stays below 10 nA. In our case, the whole process takes a few seconds and has a yield of more than 50%. Transfer from the tip to the sample is performed by positioning the tip at −2.5 V bias at the desired location and then ramping the voltage from −4.5 to −0.5 V while again decreasing the gap distance. This releasing process takes again a few seconds and the yield is slightly smaller than for the picking-up process. Both procedures can be repeated several times without breaking the tip or changing the substrate thus enabling the transfer of many molecules to different destinations.
In Fig. 4, we show an STM image with three single CO molecules adsorbed on Cu(1 1 1). Apart from the CO molecules which appear as depressions (dark spots) in the image also the well known surface standing wave patterns, as described in [7,8], can be observed. In the center of the image, a lower terrace can be seen, which splits up the topmost Cu(1 1 1) terrace. The sequence of pictures in Fig. 4 clearly demonstrates the transfer by vertical manipulation of two CO molecules (labeled B, C) from the right part of the upper terrace to its left part. During vertical transfer, the CO molecules did not dissociate, and the picking-up and putting-down of the molecules did not disturb neighboring CO molecules or change the initial tip structure. It is important to note, that while reliable lateral manipulation of CO molecules can be easily accomplished on flat Cu(1 1 1) terraces, we have not been able to laterally move CO molecules across step edges. Hence the manipulation across the lower terrace demonstrated in Fig. 4 was only possible due to our new ability to manipulate CO molecules vertically.

CO molecules on Cu(1 1 1) always appear as depressions independent of the polarity when imaged with a clean STM tip (Fig. 5, left-hand side). At positive sample bias, they are surrounded by a protruding halo. However, when imaged with a tip having a CO molecule at its apex, they appear independently of the bias polarity and voltage as protrusions, as demonstrated on the right-hand side of Fig. 5. Depending on the polarity they have a protruding halo around them or not. The shape at positive sample bias is similar to the sombrero shape found for CO on Pt(1 1 1) [22].

This inversion in shape allows us to perform chemical sensitive imaging. In the top panel of Fig. 6 part of the surface can be seen, which was exposed to \( \approx 1 \text{ Langmuir} \) of O\(_2\) at ambient temperature and subsequently cooled down to 15 K. This procedure leaves a very low level of oxygen of less than 0.1% of a monolayer on the Cu(1 1 1) surface. The oxygen atoms were found to appear as dark spots in the STM images. Subsequently the sample was exposed to low levels of CO at 15 K and again imaging was performed.

The number of depressions in the STM images had increased by a factor of six and it was hardly possible to distinguish the spots originating from oxygen from those due to CO. Picking up the dark spot indicated with the white arrow in Fig. 4 yielded a contrast reversal for most of the other dark spots while some of them (black arrow) stayed the same (lower panel of Fig. 4). The latter species could also not be picked up by the method described above. Hence we conclude that such spots originate from oxygen, while all the others, which show the change in shape due to imaging them with a CO tip, are CO molecules.

Fig. 4. STM images of a Cu(1 1 1) terrace intersected by a lower terrace imaged with 40 mV bias and 1 nA current. Three adsorbed CO molecules (labeled A, B, C) as well as surface state standing wave patterns can be seen. The CO molecule A serves as a marker. The CO molecule B was first picked up from the right part of the upper terrace, transported to the left part and put down there. The entire process was then repeated with molecule C.
Thus, by transferring CO molecules to the tip we could distinguish between different adsorbates, which are otherwise hard to keep apart. Extending this method to a larger variety of atomic and molecular adsorbates could therefore constitute a valuable tool to differentiate between a whole variety of adspecies and possibly even between different adsorption sites of chemically identical species.

A detailed analysis of the vertical transfer mechanism of CO molecules on Cu(111) shows [23], that there is a minimum tunneling bias of 2.4 V required to excite a molecule. This corresponds to the onset of the CO derived 2π⁻ level of the CO/Cu(111) system as known from two photon photoelectron spectroscopy (2PPE). The hopping rate appears to depend linearly on the tunneling current, which points to a one electron process as the basis of the excitation mechanism. The probability per tunneling electron to induce a hop of a CO molecule depends on the applied bias and has a value below 10⁻¹⁰ if the bias does not exceed 3 V. A strong isotope effect for the quantum yield of the hopping process of 2.7⁺⁰.₃⁻⁰.₅ can be found using ¹²C¹₆O and within the framework of the Menzel–Gomer–Redhead model, this isotope effect can be used to estimate a per excitation probability for a hop of a CO molecule of 5 × 10⁻⁹ and a fraction of 0.5% of the electrons making up the tunneling current passing through the level of the CO molecules [23]; the lifetime of the electrons in the antibonding 2π⁻ level is as short as 0.8–5 fs.

5. Summary and conclusions

In conclusion, we demonstrated that the pulling of a single Cu atom across a flat Cu(111) surface exhibits close classical analogies: the Cu atom stays at its site until the lateral force between the atom and the tip apex has become large enough to induce a hop to the next site. If there are additional sites on
the surface, the atom will occupy them on its way upon following the tip, even if these sites have an offset with respect to the manipulation direction, as demonstrated on the Cu(1 1 1) surface. Although on atomic scale, we thus encounter behaviours just like ping-pong balls move on tilted muffin tins.

We have furthermore proven controlled vertical transfer of CO molecules between a Cu(1 1 1) sample and an STM tip. This ability enriches the possibilities for structuring of surfaces, since molecules can be moved over surface defects like steps, which is not always possible with lateral manipulation; furthermore, build-up of structures involving the third dimension perpendicular to the surface comes into reach. In addition, with this procedure a promising route leading to chemical contrast is opened up, as demonstrated by the STM images of CO molecules and oxygen atoms obtained with bare metal and CO-functionalized tips.

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