Controlled Manipulation of Atoms and Small Molecules with a Low Temperature Scanning Tunneling Microscope

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Abstract

With the scanning tunneling microscope (STM) it became possible to perform controlled manipulations down to the scale of small molecules and single atoms, leading to the fascinating aspect of creating manmade structures on atomic scale. Here we present a short review of our work in the last five years on atomic scale manipulation investigations. Upon soft lateral manipulation of adsorbed species, in which only tip/particle forces are used, three different manipulation modes (pushing, pulling, sliding) can be discerned. We show that also manipulation of highly coordinated native substrate atoms is possible and demonstrate the application of these techniques as local analytic and synthetic chemistry tools with important consequences on surface structure research. Vertical manipulation of Xe and CO is presented, leading to improved imaging and even chemical contrast with deliberately functionalized tips. For the transfer of CO it is shown that beside tip voltage current effects play also an important role. This is also the case for the dissociation of molecules. With CO transferred deliberately to the tip we have also succeeded to perform vibrational spectroscopy on single molecules. Furthermore, first experiments aiming for the transfer of all manipulation modes to thin insulating films are described.

Introduction

The scanning tunneling microscope (STM) was initially intended for imaging surfaces and has proven in many surface science problems its unique abilities in producing images down to atomic resolution. It was soon realized that - upon scanning - the tip often influences the surface due to the close proximity of the tip to the surface atoms. This obvious disadvantage for imaging was, however, readily turned into a positive prospect by realizing that the modifications could perhaps be made in a controlled way. Pertinent studies showed that the STM indeed offers startling possibilities to modify surfaces down to the nm- and even to the atomic scale [1-3]. Thus, the longstanding engineering dream of building up man-designed functional structures and to create new material combinations or even new materials in an atom-by-atom manner appear to have come into realistic reach.

The three main parameters which can be applied for STM surface modifications are the electrical field between tip and substrate, the tunneling current and the forces between tip and surface [2]. On working with single atoms and molecules, we distinguish lateral and vertical manipulation modes. In the former mode, a particle on the surface is moved along the surface to the desired place without loosing contact to the substrate, in the latter mode a particle is deliberately picked up by the tip and released back to the surface. These two transfer modes are
schematically illustrated in Fig. 1. Although field and current effects can be used for lateral manipulation, too, reliable precision on atomic scale is achieved with "soft manipulation" in which mainly the tip-substrate forces, which can be tuned via the distance between the tip and the manipulated particle, are employed.

Fig.1. Idealized sketches of (a) the pulling procedure in lateral manipulation of single atoms or molecules on a Cu(211) surface (lateral manipulation) and (b) of the picking-up and putting-down procedure of a Xe atom (vertical manipulation).

Experimental

In all our experiments we used self-built, versatile STM's capable of operation between 8 and 300 K. A detailed description of the first self-built instrument can be found in Ref. [4]. As substrates for our manipulation experiments we used the closely packed (111) and the regularly stepped (211) surfaces of Cu, which consists of (111)-nanofacets separated by (100)-steps of monoatomic height. The crystals were prepared in UHV by several cycles of sputtering with Ne-ions and annealing at about 700 K. Very low coverages of gaseous adsorbates were prepared by dosing through a very fine hole to the sample located in the STM in the first system and in a separate preparation chamber in the newer setup. Metals were evaporated from Knudsen cells in analogous ways.

Results and Discussion

Lateral Manipulation

Fig. 2. (a) STM images of the logo "FU" designating the Free University of Berlin as an example of an early attempt to build man-made structures and (b) of the millennium number "2000" as a very recent example of lateral manipulation. In both cases CO molecules were used. Note that perfect precision on atomic scale is achieved for the "2000" upon locating 47 molecules. Substrate temperature for (a) 40 K and for (b) 15 K. Image size (a) 6nm x 12nm (b) 24nm x 24nm.

In Fig. 2 we contrast our early (1994) ability [5] to create artificial structures with the present state of the art. Whereas the letters "F" and "U", which constitute the logo of our university suffer from small irregularities, the symbol "2000" heralding the beginning of the new millenium is perfect on atomic scale. In both cases CO molecules were manipulated laterally on Cu(211), whereby for the "2000" a total of 47 molecules was necessary to build up the structure. Our early experiment was performed at 40 K, where thermal agitation of the weakly chemisorbed CO forces the experimentalist to fight continuously against entropy, and the recent work was done at 15 K, where the
molecules are frozen in to a sufficient degree, so that precise working is possible with a rather large number of particles and the artificial structure remains stable. An impression concerning different stages of the buildup work of an artificial structure like the '2000' is given in Fig. 3.

After having successfully manipulated small molecules like CO and C2H4, we also proved manipulation of atoms such as Pb and Cu, whereby increasing forces (as measured qualitatively by the decreasing tunneling resistance) had to be applied in the respective order. With still increasing forces, we showed on Cu(211) that it is also possible to release native substrate atoms from sixfold coordinated kink sites (Fig. 4a-c) and even from sevenfold coordinated regular step-edge sites (Fig. 4d-f). This important result opens the way for structuring the surface itself with the promising prospect that also deeper lying substrate layers may be included in the build-up of artificial prototype structures. We could also show that vacancies at step edges of regularly stepped surfaces like Cu(211) can be "healed up" by manipulating single atoms into the edges [6].

An important example of an application of the ability to release substrate atoms from their surrounding neighbours by lateral manipulation concerns analytical chemistry on atomic scale: Deposition of Pb at room temperature onto Cu(211) leads to a regular overlay consisting of rows along the intrinsic step edges with a periodicity of 3 copper nearest neighbor distances. As it was not clear whether these rows consisted of Pb atoms alone or whether surface alloying had taken place, we removed from the end of a row one atom after another to an adjacent substrate area not covered by foreign atoms, where we could identify them as alternating Pb and Cu atoms; thus, a PbCu surface alloy...
forms at elevated temperatures. This proves that the
technique of working into the substrate in an atom by atom
manner can be used for *chemical analysis on atomic scale*.
The structure presented in Fig. 5 shows the formation of a
quantum corral by lateral manipulation of Ag atoms on a
Ag(111) surface, similar to the ones first created in Eigler’s
group. The atoms have been positioned in a circular
geometry with a diameter of 22nm. The electrons in the
surface state are scattered by the Ag atoms resulting in a
circular interference pattern. The observed standing wave
pattern becomes highly sensitive to the phase relaxation
length of the electrons if the diameter of the corral is of
comparable size [7,8]. In this context these corrals may be
thought of as nanoscale quantum laboratories.

**Pulling, Pushing and Sliding of Atoms and Molecules**

In further work with Cu-atoms, Pb-atoms and CO-molecules
on Cu(211) we could distinguish different manipulation
modes in dependence of the tip-particle force (again
measured in a qualitative way by the tunneling resistance)
as demonstrated in Fig. 6: Pb- (and also Cu-) atoms could
be manipulated via attractive tip-adatom interactions in a
way in which they follow the tip discontinuously by hopping
from one adsite to the next (pulling mode, Fig. 6a).

Upon application of larger forces than for pulling, Pb-
atoms could also be manipulated attractively in a
continuous way (sliding mode, Fig. 6b); in this mode the tip-
particle interaction is increased so strongly that the tip-
particle system scans the corrugation of the substrate,
whereby, however, also the particle substrate interaction is
still strong enough to keep the particle on the substrate.
Finally, single CO-molecules as well as rows of several CO-
molecules were found to be manipulated reliably via
repulsive interaction (pushing mode, Fig. 6c), whereby the
intrinsic step edges, on top of which the CO-molecules are
bound, act as railway trails [9]. Due to the repulsive
interactions also entire rows of CO adparticles can be
moved at once as demonstrated in Fig. 7.

**Vertical Manipulation**

Vertical manipulation was first observed by Eigler, who
demonstrated an atomic switch by transferring repeatedly a
Xe atom from the surface to the tip and vice versa. In our
experiments with Xe we chose another way to prove
successful transfer of Xe to the tip: We used the tip with the
Xe atom sitting at its apex for imaging the same area (Fig.
8b) as before with the bare tip (Fig. 8a). Noticeably, the
resolution is markedly improved showing that the single Xe
atom “sharpens” the tip. In Fig. 8c the resolution is the
same as initially, as the Xe atom has been transferred back
to the surface, however to another place than the initial one.

*Fig. 6. Tip height curves during manipulation of (a) and (b) a Pb-atom and (c) a CO-molecule along step edges on Cu(211). The tip is moved from left to right and respective tunneling resistancies are indicated. The vertical dotted lines correspond to fcc sites next to the step edge. The initial sites of the manipulated particles are indicated. Notice that in the attractive manipulation modes (a: pulling and b: sliding) the particles first hop towards the tip and then follow it, whereas in the repulsive mode (c: pushing) the particle performs hops away from the tip.*
Fig. 7. Demonstration that for the repulsive mode of lateral manipulation as observed for CO on Cu(211) entire rows of molecules may be manipulated at once. Notice that after manipulation the molecules in the row exhibit the ideal distance of two substrate nearest neighbor distances, which is characteristic for the first ordered CO-adlayer on this surface.

A very advantageous byproduct of the ability to transfer CO to the tip deliberately is demonstrated in Fig. 9b,c. Whereas all species imaged with a clean metal tip appear as depressions, with the CO-molecule denoted by the white arrow transferred to the tip apex all CO molecules change their appearance to protrusions (Fig. 9c), whereas the oxygen atom in the upper left part of Figs. 9b,c retains its appearance [10]. Thus, we have achieved chemical contrast in STM imaging, a phenomenon very useful for the analytic abilities of the STM.

The understanding of the dependence of images on parameters like the chemical constitution of the tip or the density of adsorbed species on the surface is, however, still a formidable question as can be realized from Fig. 10 [11]. In Fig. 10a we show a regular adlayer of CO on Cu(211) with (3x1) periodicity. With the knowledge of the coverage of 2/3 of a monolayer, a structural model like the one illustrated in Fig. 10b, where CO molecules occupy on-top and bridge sites thus maximizing their mutual distance appears plausible. In Fig. 10c-e we show, however, that laterally manipulating together two CO molecules into adjacent on-top sites changes the image from two minima into one maximum located between the two on-top sites. Thus upon formation of a CO-“dimer” a dramatic change in the appearance of the two CO molecules has occurred (Fig. 10d). By separating the two CO molecules their appearance changes to the initial shape. Using the lateral manipulation technique we can form also an extended domain of the (3x1) structure (Fig. 10f) leading to the conclusion that the model depicted in Fig. 10g is the proper one and has to replace that of Fig. 10b. It is worthwhile noting, that the formation of a domain of a regular adlayer of a foreign species in a particle by particle manner can be regarded as a first example of chemical synthesis on atomic scale.

Fig. 8. Vertical manipulation of a Xe atom. The Xe shows up as a bright hill in (a). In (b) the Xe has been picked up with the tip and the STM scan is performed with the Xe at the tip apex. Noticeably, the Cu(211) surface is now imaged with much better resolution. In (c) the Xe atom has been released at another place back to the surface and the imaging is done with the initial resolution.
Vibrational Spectroscopy with the STM

Whereas spectroscopy of electronic states employing the STM is used since more than 10 years, vibrational spectroscopy was pioneered only in 1998, when the group of W. Ho [12] showed that the C-H stretch mode could be observed on single C2H2 molecules adsorbed on a Cu(111) surface. Later the CO frustrated translational and rotational modes [13] as well as the internal stretching mode were observed on Cu(100) and Cu(110) [14]. Upon working with a tip onto which a single CO molecule was transferred by vertical manipulation, we could also observe the frustrated rotational and vibrational modes of CO on Cu(211) with energies at 5.8 and 35.9 meV, respectively, as shown in Fig. 11 [15].

Effects Due to Electron Current

A detailed analysis of the vertical transfer mechanism of CO-molecules on Cu(111) showed [16], that a minimum tunneling bias of 2.4 V is required to excite a molecule. This corresponds to the onset of the CO derived 2σ*-level of the CO/Cu(111) system as known from two photon photoelectron spectroscopy (2PPE). The hopping rate depends 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 3V. A strong isotope effect for the quantum yield of the hopping process of 2.7 ± 0.3 can be found using ^12C16O and ^13C18O. 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 2σ*-level of the CO-molecules; the lifetime of the electrons in the antibonding 2σ*-level is as short as 0.8 - 5 femtoseconds [16]. Thus, the CO-transfer depends on an effect induced by the electrons provided by the tunneling current. The approach of the tip in the pick-up procedure just increases the probability, that the molecule is "caught" at or near the tip apex [10].
Electron current effects play also an important role in the dissociation of molecules [2]. By combining all hitherto known techniques of working with single atoms and molecules, we were recently able to induce all steps of a complex chemical reaction with the STM tip at low temperature, at which the reaction would not proceed naturally. Specifically, we prepared the reactants (phenyl) from the starting chemicals (iodobenzene) by electron stimulated dissociation, removed the split off iodine atoms from the path between two reactants by lateral manipulation, brought two reactants together again by lateral manipulation and showed that the reaction (to form biphenyl) was not induced due to the proximity of the two species alone by pulling from one side and observing that one reactant followed but the other stayed behind. We further showed that upon electron stimulus the association of the two reactants takes place and proved the stability of the product by pulling the entire species [17].

Towards Manipulation on Insulating Substrates

With respect to the build-up of man-designed functional structures the ability to manipulate atoms and molecules requires extension to nonconducting substrates, so that manipulation techniques feasible with the atomic force microscope are a very important goal. With regard to the different possibilities achieved with the STM, an important intermediate step in this direction certainly is the attempt to transfer all the structuring techniques on surfaces described in this survey to thin films of insulating materials on metallic substrates. For this purpose, we have started to study the growth of LiF on Ag(111) [18] and NaCl on Cu(211). Whereas the first system yields fractal growth and is therefore not prospective for our purpose, we observe for NaCl/Cu(211) at temperatures below 200 K the growth of chainlike NaCl islands with monoatomic height as modeled in Fig. 12 [19]. An atomically resolved image of such a chain is shown in Fig. 12b. Obviously only one constituent of NaCl can be observed, the Cl-ions [20]. Fig. 12c-e show that these chains can be cut by the lateral manipulation technique whereby the entities are pushed (Fig. 12f). It is also possible to release single molecules from these chains and to manipulate them onto the free parts of the Cu(211) substrate. Interestingly, NaCl deposition at substrate temperatures > 300 K [21] leads to faceting into (311) and (111) facets whereby NaCl grows selectively on the (311) facets, so that alternating stripes of bare Cu and NaCl covered areas are formed. Depending on growth temperature the width of the stripes can be varied between 3 and 23nm. Surfaces structured in this way bear interesting potential for the fabrication of e.g. magnetic...
nanostructures. The fact that the (311) facets of the faceted Cu(211)-surface are covered by NaCl led us to investigations of NaCl on Cu(311): As expected, flat thin films of NaCl can be grown on this metal substrate, so that the aim outlined at the beginning of this section is coming into reach.

**Resume**

In this presentation, we discussed lateral manipulation of atoms and small molecules on solid substrates with the technique of “soft” manipulation in which basically tip-particle forces are employed. Detailed analyses of vertical manipulation show, that beside tip/particle forces also electronic effects are important for the transfer of particles like CO and Xe from substrate to the tip and vice versa. Electric current effects also play dominant roles in STM-induced chemical changes of molecules like dissociation [2]. A combination of all parameters (forces, current, field) is required for the association of several species to yield a new chemical entity. Thus engineering with single molecules and even single atoms in the sense, that novel manmade functional structures or even novel artificial molecules can be made, appears no longer to be a mere utopia.

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