Scanning Tunneling Microscopy Manipulation of Native Substrate Atoms: A New Way to Obtain Registry Information on Foreign Adsorbates

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We demonstrate successful lateral manipulation of host atoms on Cu(211): In a controlled manner we are able to release Cu atoms from upper terraces, move them on the lower terrace to form dimers and trimers, and adhere them to the terrace edge again. We apply this novel ability to deduce information on adsorption sites of foreign species: By bringing Cu atoms close to CO molecules, we determine the location of the adsorbate. The sites of C_2H_4 and Pb are then found via coadsorption with CO. [S0031-9007(96)01077-0]

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The stability and precision of modern scanning tunneling microscope (STM) systems allow positioning of the tip on subnanometer scale and have thus stimulated diverse efforts on surface modifications in the nanometer and even atomic range, as recently reviewed by Avouris [1]. The possibility to laterally move individual adatoms in a controlled manner on solid surfaces and to build man-made structures on nanoscale [2], as well as to transfer Xe atoms vertically from the substrate to the tip and back [3] at 4 K, was first demonstrated by Eigler and collaborators. With a versatile low-cost temperature variable STM that can be operated between 15 and 300 K [4], we have recently proven our ability to perform lateral manipulation of single CO molecules and to build up prototypic nanostructures [5], as well as to manipulate single Xe atoms vertically [6] on a Cu(211) surface. As an important further step for surface structuring on an atomic scale, we show here that we are now also able to perform controlled lateral manipulation with atoms of the substrate host. We can release Cu atoms from upper terraces, although they are strongly bound due to their high coordination number. We can then move these atoms to desired places, form little clusters with them, and adhere them again to the terrace edges. An important first application of this new technique concerns one of the key issues in surface science, namely, the determination of binding sites of adparticles. We move substrate atoms close to adsorbed CO molecules and infer from the natural location of the single Cu atom the registry of the adsorbate with respect to the substrate lattice. The so determined location of CO is then used to deduce the adsorption site of coadsorbed C_2H_4 . Obviously, this new technique will be of great importance not only in structuring of surfaces in the subnanoscale, but also in determining adsorption sites on complex high index surfaces with large unit cells, which are presently of great interest, but not amenable to conventional surface crystallographic methods [7].

The STM experiments are performed in a UHV chamber with a base pressure $<2 \times 10^{-10}$ mbar, which is equipped with low energy electron diffraction (LEED) and a low

temperature STM located in a special cryostat [4]. After preparation of the surface by repeated cycles of sputtering and annealing, the sample is transferred into the 4 K cryostat containing the STM, where it is cooled to a temperature between 15 and 80 K. In adsorption experiments the sample is exposed to the desired gaseous species through a small hole in the radiation shields. As the small hole leaves only a small solid angle for adsorption, partial pressures higher by factors >3000 have to be used to obtain coverages equivalent to those in which the sample is exposed outside the cryostat. Dosing inside the cryochamber has the important advantage that the contribution of residual gases is extremely low; thus in the STM experiments the surface cleanliness is very good and very small amounts of adsorbates can be studied without contamination. The temperature in the STM chamber is determined with a Sidiode sensor close but not in direct contact with the sample. For taking STM images tunneling currents between 100 pA and 5 nA were used in all experiments described below. Bias voltages refer to the sample voltage with respect to the tip. The topview of a sphere model of the clean Cu(211) substrate is shown in Fig. 1 with the deepest lying substrate atoms shaded darkest: The surface consists of (111) terraces separated by (100) single steps. Apart from these intrinsic steps there are always defect steps, which separate two neighboring (211) terraces. Such defect terraces, which have a height difference of 0.074 nm, are indicated in Figs. 1(a) and 1(b) by the brightest Cu spheres. In all STM pictures shown, the surface orientation is (apart from some tilt) the same as the one indicated in Fig. 2(a). The surface was prepared by several cycles of sputtering with 800 eV Ne ions and annealing to 800 K. As STM tips we used electrochemically etched tungsten wire. The substrate temperature varied between 20 and 30 K in all STM images shown.

In Fig. 2 we demonstrate the intentional removal of single host atoms from the edge of an upper terrace. In order to display the lower terrace with optimum contrast, the higher terrace appears fully white in the STM pictures. In Fig. 2 individual Cu atoms are removed from the row of



FIG. 1. Sphere model of the Cu(211) substrate; the Cu atoms are shown as small spheres with the deepest lying atoms shaded darkest. A grid of surface unit cells is plotted ($|a_1| = 0.625$ nm; $|a_2| = 0.255$ nm). The ideal surface consists of (111) nanoterraces and (100) steps. In (a) and (b) higher lying defect (211) terraces are indicated via the brightest Cu atoms, illustrating the situations of Figs. 2(a) and 4(a), respectively. In (b) the location of a single Cu atom is indicated together with the location of a CO molecule, which has been determined from Fig. 4(c). The location of ethen and Pb relative to CO as determined in coadsorption experiments (see text).

the upper terrace in which several atoms protrude farther to the right than on the adjacent rows [the situation is modeled in Fig. 1(a)]. In Fig. 2(a) the single atom denoted by the white arrow has already been moved away along $[01\overline{1}]$ from the kink site in this row in the direction of the black arrow; in Fig. 2(b) a second Cu atom has been released and brought close to the first one. In Fig. 2(c) both Cu atoms are moved further away, and in Fig. 2(d) a third atom is removed from the upper terrace. In Fig. 2(e) two atoms are brought together to form a dimer. In Fig. 2(f) all three atoms have been moved together to form a linear trimer. The dashed line in Figs. 2(a)–2(f) denotes the edge of the upper terrace row after one atom had been removed; notice that the row becomes shorter upon removal of two further Cu atoms.



FIG. 2. Releasing single Cu atoms from a higher defect terrace. (a) A single Cu atom indicated by the white arrow was released and moved according to the black arrow [see model in Fig. 1(a)]. (b) A second Cu atom is released. (c) Both atoms are moved farther away from the defect step along $[01\overline{1}]$. (d) A third atom is released. (e) Two Cu atoms are manipulated to form a dimer. (f) The three Cu atoms are forced to build a trimer.

The technique we applied for lateral manipulation is analogous to the sliding technique employed previously [3,5]: Whereas in the STM imaging process the tip is scanned at distances of a few atomic diameters above the surface and—in the constant current mode—follows contours of constant electronic density of states, for the manipulation process the tip is brought close to the surface by reducing the tunneling resistance and is then moved parallel to the surface by a pregiven distance whereby the atom is dragged (or pushed) to the desired place. There the tip is drawn back to the scanning distance and a new STM picture is taken to check the result of the manipulation.

Cu atoms located in kink sites have 6 nearest neighbor atoms. Thus, these atoms have a much higher binding energy than adatoms on flat substrates like (111) surfaces where they have only 3 nearest neighbors [3]. To remove native Cu atoms from kink sites, consequently a high lateral force has to be employed, meaning that the tip must be brought very close to the substrate. A measure for the distance between sample and tip and thus a measure for the force is the tunneling resistance [8]. The tunneling parameters for removal of Cu atoms from the upper terrace are $I_t = 1.5 \ \mu A$ and $U_t = +0.13 \ V$. This corresponds to a tunneling resistance of only $80-90 \text{ k}\Omega$ (note that the resistance at point contact is $h/2e^2 = 12.9 \text{ k}\Omega$ [9]). For comparison we mention that lateral manipulation of CO molecules on Cu(211) requires resistances of $\sim 1 M\Omega$. One important factor to discuss in connection with the loosening of the substrate atom bonds is the shape of the tip. As one recognizes from Fig. 2, the appearance of the isolated Cu atoms is not symmetric, indicating that the tip is definitively not as sharp as tips yielding optimal resolution; i.e., it is certainly not an ideal oneatom tip. This is simply due to the fact that tips yielding excellent images usually do not survive the strong forces involved in manipulating substrate atoms. Consequently, tips suited for substrate modifications are probably not ideal for imaging and vice versa.

We now turn to the determination of the adsorption sites of CO molecules on Cu(211). As we have shown in a previous study, all CO molecules in dilute concentrations occupy equivalent sites [10] on the close packed rows at the step edges of the (111) facets; the same sites are also occupied in the first ordered (2×1) phase [10]. The location along the $[01\overline{1}]$ direction remained, however, uncertain. In Fig. 3 we show that with specially prepared tips it is possible to observe single CO molecules while resolving the substrate step edges with atomic resolution. The single depression corresponds to a single CO molecule [11]; the line drawn through the molecule perpendicular to the steps passes through maxima of the substrate corrugation. A naive interpretation would assign these maxima to underlying Cu atoms, implying that the CO molecule occupies a top site. We know, however, from beam diffraction experiments [12] that even for the most inert He atoms anticorrugating effects play an important role and can shift corrugation maxima to bridge sites along close packed metal rows; interestingly, anticorrugating effects are negligible for Ne [12]. As tip/surface interactions are undoubtedly more complicated than rare gas/surface interactions, anticorrugating effects cannot be ruled out in STM experi-



FIG. 3. STM image of a CO molecule (depression) obtained with atomic resolution of the substrate. The observed corrugation in the STM image along the close packed Cu rows is 1.5 pm and across the rows 23 pm.

ments. Indeed a recent STM experiment on the Fe(100) surface has shown anticorrugating effects [13]. With this in mind we used our new manipulation technique to determine the registration between single Cu atoms and CO molecules along $[01\overline{1}]$.

Figure 4(a) shows an STM image with a single Cu atom and several CO molecules; in this case the CO molecules appear as small bumps [11]. The mesh size of the grid plotted in Fig. 4(a) corresponds to that of the Cu(211) unit cell; its lateral position is chosen such that the grid lines cross at the CO's [14]. Notice that the single Cu atom is shifted by half a lattice constant along $[01\overline{1}]$, implying that the CO molecules reside in on-top positions along the close packed rows at the step edges. At the temperatures used in our experiments, the Cu atom occupies its natural bulk-like fivefold coordinated site at the step edge, as illustrated in Fig. 1(b). It is important to realize that the center of symmetry of the CO image is used in evaluating the CO location, because according to Fig. 3 CO lies on a mirror plane perpendicular to the step edges. Our previous observation that the actual shape of the CO can vary significantly with tip composition, therefore, does not disturb the adsorption site determination.



FIG. 4. The Cu atom indicated has been released from the terrace and transferred close to a CO molecule. From the location of the single Cu atom, the CO location is determined. The grid is plotted to ease the proper assignment [see model in Fig. 1(b)]. (b) The single Cu atom is transferred back to its initial place along the black arrow. (c) The Cu atom is reattached to the defect terrace. Because of the broad tip also, the CO molecules near the Cu atom were affected by the manipulation.

The above discussion tacitly assumed that the ridges in the images correspond to the step edges. As anticorrugating effects can also not be ruled out *a priori* in the direction perpendicular to the steps, although the corrugation amplitude along this direction is appreciable larger than parallel to the steps, again the study of single substrate atoms is helpful. Line scans along [111] reveal that the maxima of the ridges are shifted by $a_1/3$ against the maximum corresponding to a single Cu atom (or a row of a few Cu atoms); this proves that the maxima of the ridges correspond to the step edges. Thus, the maxima in the substrate corrugation of Fig. 3 correspond indeed to Cu atoms along the close packed step edge.

The single Cu atom used for registry determination of the CO molecules in Fig. 4(a) had actually been released before from the upper terrace visible at the right-hand side. In Figs. 4(b) and 4(c) we demonstrate the reattachment of the Cu atom to its original site at the edge of the upper terrace. That broad tips and low tunneling resistances used for substrate atom manipulation as discussed above are manifested in these pictures, as they show that not only the Cu atom was moved to its original place, but that also the CO molecules in adjacent positions were affected. This is probably due to the fact that since CO molecules can be manipulated with a much smaller force, other parts of the tip might be still close enough to drag along adjacent CO molecules. Notice especially that the CO molecule sitting initially on the lower terrace close to the upper one was actually forced to step up to occupy a site at the edge of the upper terrace.

The known CO location can now be used as an alternative marker instead of a native Cu atom. By coadsorbing CO with ethen and lead, we have determined that the center of a single ethen molecule is located over a twofold bridge site at the step edge and that single Pb atoms are located in the same high coordinated sites as single Cu atoms. These results are indicated in Fig. 1(c).

In conclusion, we have demonstrated our ability to remove single native substrate atoms in a controlled manner from strongly bound defect terrace kink sites by using a lateral STM manipulation technique. Apart from using the substrate atoms to build nanostructures, we prove their usefulness as markers for determinations of foreign adsorbates. CO was determined to occupy on top positions at the step edge, while C_2H_4 lies parallel to the step edges with its center above a twofold bridge position. Considering the presently increasing interest in complex high index surfaces with large unit cells, which are still difficult to tackle with the conventional surface crystallographic methods, our new tool of "forced coadsorption" of native substrate atoms with foreign species will certainly constitute a valuable aid for future quantitative surface structure determinations. The extension of our new technique of manipulating native substrate atoms to other materials, especially to surfaces of technologically relevant semiconductors, is presently under investigation.

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