Controlled Atom by Atom Restructuring of a Metal Surface with the Scanning Tunneling Microscope

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We report the ability to completely restructure a metal surface by precision manipulation of individual atoms with the scanning tunneling microscope: Besides extracting atoms from kink sites on Cu(211) we are now also able to "dig out" atoms from the even more strongly bound intrinsic step sites and thus to create adatom-vacancy pairs. Together with the processes of moving adatoms along and across intrinsic step edges and the possibility of healing out adatom-vacancy pairs, we have a complete set of lateral manipulation processes at hand. The reliability of all these processes opens up exciting "engineering" possibilities for structuring of extended surface areas. [S0031-9007(97)02523-4]

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The present intense activity in structure formation at surfaces by using the tip of a scanning tunneling microscope (STM) has yielded promising results in the nanometer and subnanometer range. Certainly one important achievement is that single atoms and molecules can be studied and manipulated with atomic scale precision [1,2]. To do this, different physical and chemical interaction mechanisms between tip and sample are exploited. Because of strong directional bonds the techniques used in the atomic modification of semiconductor surfaces up to now employ the effects caused by the electric field between tip and sample or by the current flowing through the gap region [1,3]. Most of the work on metal surfaces, however, used solely the forces that act on an adsorbate due to the proximity of the tip [4,5]. Large molecules have been manipulated at room temperature using strong repulsive forces [6]. As single metal adatoms or small molecules are mobile at ambient temperatures, experiments on small adsorbates located on low index metal surfaces have been conducted at low temperatures using the sliding technique [2,5]. One major advantage of the sliding technique is its excellent precision and reliability, which up to now culminated in the formation and physical characterization of quantum corrals by Crommie *et al.* [7]. In this Letter we concentrate not on the manipulation of single adatoms but on modifications of the substrate itself, which are expected to be more difficult due to the higher coordination number and binding energy of atoms located in the surface or in steps. Attempts to manipulate single substrate atoms were up to now reported with field evaporation techniques [8–10] and it has been shown that at room temperature by tip assisted diffusion monoatomic steps can be displaced over appreciable distances [11]. In a recent Letter we already demonstrated that with the atom sliding technique we can extract in a controlled manner atoms from kink sites and move them along the intrinsic step edges [12]. Here we go a significant step further and present a complete set of manipulation processes with which a restructuring of Cu(211) (and very likely of similar stepped surfaces) on an atom by atom basis becomes possible. Our novel manipulation processes include the movement of native substrate atoms across intrinsic step edges, the controlled extraction of single substrate atoms out of intrinsic steps, as well as the healing of vacancy sites.

Our experiments were performed with a low temperature STM [13] operated at 30–40 K. These temperatures are low enough to quench the mobility of single Cu atoms on Cu(211). For taking the STM images tunneling currents between 100 pA and 5 nA were used. Bias voltages refer to the sample voltage with respect to the tip. As STM tips we used electrochemically etched tungsten wire.

The structure of the Cu(211) substrate is displayed in Fig. 1 via the top view of a sphere model, whereby the atoms are shaded darker the deeper they lie. The ideal surface consists of (111) terraces separated by (100) single steps. Apart from these regular intrinsic steps defect steps are present on the surface which separate two neighboring (211) terraces at a vertical distance of 0.0745 nm. Such a defect terrace is indicated in Fig. 1. In all STM pictures shown the surface orientation is the same as in Fig. 1. Note that the bright lines in the STM pictures correspond to the close-packed Cu rows at the step edges [12].

In the following we demonstrate in the order of increasing difficulty all the different manipulation processes we are able to perform with native atoms on Cu(211); the different procedures are indicated in Fig. 1 and denoted by small letters. In Figs. 2(a)–2(c) we show the lateral manipulation of a single Cu atom parallel and perpendicular to a step. In Fig. 2(a) a single Cu atom is located in the lower half and a second Cu atom in the upper half, which serves as a marker. The arrow indicates the distance and direction along which the lower single Cu atom is manipulated along the step edge (process a in Fig. 1). The result is shown in Fig. 2(b). The same atom is then transferred over the step edge along the $[1\bar{1}\bar{1}]$ direction as proven in Fig. 2(c). The latter manipulation corresponds to "step down" motion (process b, Fig 1); "step up" manipulation (process c, Fig. 1) is also feasible [14].

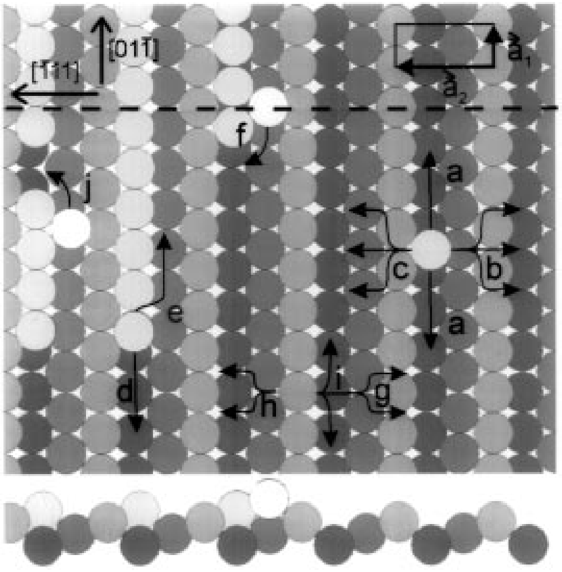

FIG. 1. Top and side views of a sphere model of the Cu(211) substrate; the Cu atoms are shown as small spheres with the deepest lying atoms shaded darkest. The side view corresponds to the dashed line plotted in the top view. The surface unit cell vectors are indicated ($|a_1| = 0.255$ nm, $|a_2| = 0.625$ nm). The ideal surface consists of (111) nanoterraces and (100) intrinsic steps. A higher lying (defect) terrace is indicated in the left part to illustrate the situation in Fig. 4. The different manipulation procedures realized experimentally are indicated by small letters.

The technique applied for lateral manipulation is analogous to the sliding technique employed previously [4,5]: Whereas in the STM imaging process the tip is scanned at distances of a few atomic diameters above the surface, for the manipulation process the tip is brought close to the surface by reducing the tunneling resistance. The latter is a measure for the distance between sample and tip and thus a measure of the force [15]. The minimum force necessary to move an atom corresponds to a threshold tunneling resistance. The resistances given in this Letter are close to threshold values. The tunneling resistance used in Figs. 2(a)–2(c) was ~700 kΩ for moving Cu atoms along the step edge and ~500 kΩ for moving them over the step edges. For comparison we note that lateral manipulation of CO molecules on Cu(211) requires resistances of about 1 MΩ [5]. (Notice that the resistance at point contact is $2e^2/h = 12.9$ kΩ.)

Figures 3(a)–3(c) show that we can "dig out" native copper atoms from even higher coordinated sites than the kink sites discussed recently (processes *d* and *e* in Fig. 1) [12], namely, step sites with sevenfold coordination located in the intrinsic steps, which form the topmost layer of the ideal (211) surface. Figure 3(a) shows an area on Cu(211) with a single Cu atom as a marker. Figures 3(b) and 3(c) demonstrate the extraction of single atoms in the step down direction and deposition at the edges of the adjacent intrinsic steps (process *g* in Fig. 1). The corresponding vacancies remaining in the initial sites of the atoms are clearly visible. The fact that there is a one to one correspondence in the number of adatoms and vacancies proves that each adatom is really detached from the substrate and not from the tip. For manipulation process *g* the tunneling resistance had to be reduced to ~70 kΩ. We note that it is also possible to detach step atoms in the step-up direction (process *h*, Fig. 1) and that by moving the tip perpendicular to the steps over a larger distance process *h* can be performed several times at a single stroke.

In Figs. 3(d) and 3(e) we show the creation of an adatom-vacancy pair via process *i* of Fig. 1 and in Fig. 3(f) we demonstrate the possibility of filling the vacancy with the adatom via process *j* of Fig. 1. We point out a new interesting observation: A larger force is needed to bring the Cu atoms into the vacancies than to move them along the close-packed rows; this points to a local buildup of a Ehrlich-Schwoebel barrier [16] and raises the hope that in the future quantitative measurements on local barriers will become possible.

On the Cu(211) surface the above demonstrated manipulation procedures form a complete set with which atom by atom structuring of the surface is possible. Substrate atoms located in fivefold, sixfold, and even sevenfold coordinated sites can be manipulated. It is important to recognize that in all cases we use only attractive

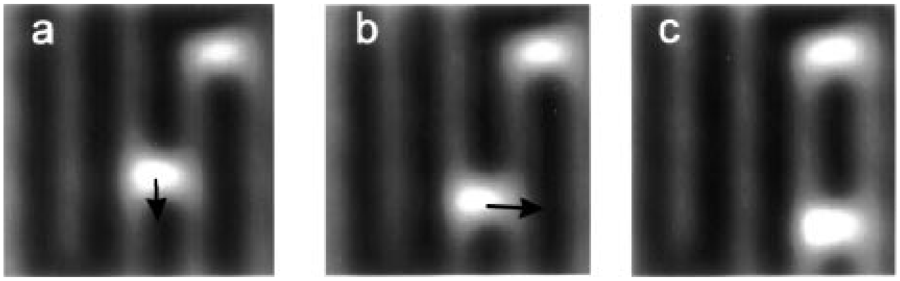

FIG. 2. (a)–(c) Lateral manipulation of a single Cu atom parallel and perpendicular to a step. The intended motions are indicated by arrows. The second single Cu atom in the upper half serves as a marker. The processes involved correspond to *a* and *b* in Fig. 1. The sample bias voltage for procedure *a* was 100 mV and for *b* 70 mV. The current used for manipulation was 175 nA and for imaging 1.75 nA.

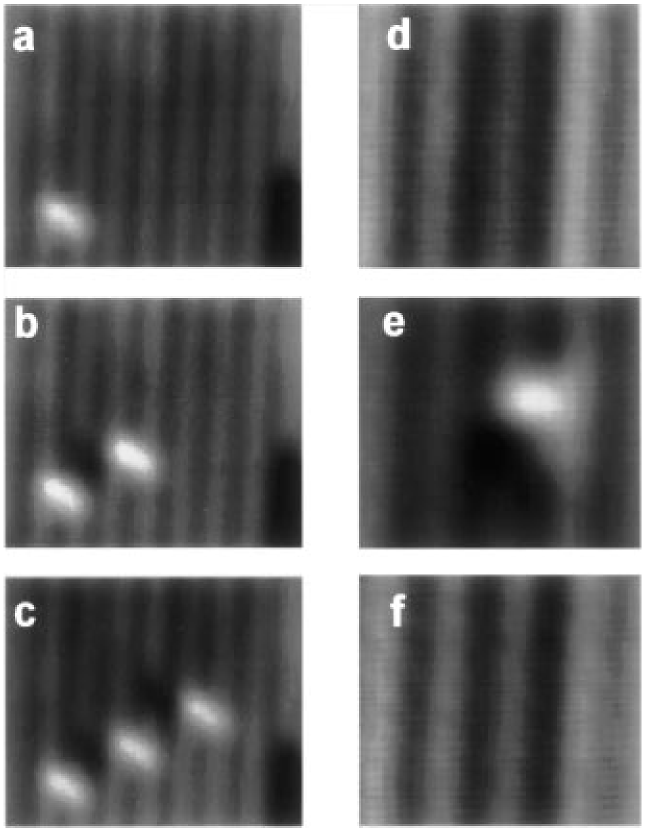

FIG. 3. (a)–(c) Two copper atoms are dug out one by one from intrinsic steps according to procedure *h* in Fig. 1. The single isolated atom in (a) serves as a marker. The sample bias voltage was 12 mV. The current used for manipulation was 130 nA and for imaging 1.35 nA. (d)–(f) Creation of an adatom-vacancy pair via process *i* in Fig. 1 (*e*), and filling of the vacancy with the adatom via process *j* in Fig. 1. The sample bias voltage was 12 mV. The current for manipulation was 130 nA and for imaging 1.35 nA.

forces between the substrate atoms and the tip. This important result is indicated by the fact that the tunneling resistance (although it can vary by a factor of 2 depending on the actual tip shape) is always significantly above the resistance for point contact. Additionally no transfer of substrate atoms between the substrate and the tip or vice versa is observed. Moreover, process *g* applied in Figs. 3(a)–3(c) uses the same tip apex to extract a single atom from the step and to transport it across a neighboring step edge. With repulsive forces one would not be able to move atoms across a step edge. From all this we conclude that also this above process belongs to the category of attractive manipulation processes as the ones previously referred to the so called sliding technique [2,4]. This is a remarkable fact since the binding energy of substrate atoms can be quite high. Unfortunately no calculations or diffusion data are available for the Cu(211) surface. Therefore as an estimate we refer to effective medium theory calculations of surface defects on Cu(111) [17]. These show that the activation energy for diffusion of atoms out of intrinsic steps onto the terrace amounts to 0.770 eV, which is much higher than the energies for diffusion of atoms out of kink sites and across and along step edges, which are 0.438, 0.365, and 0.228 eV, respectively. A few factors might help to surmount this high energy barrier. One is that the above energies constitute only an upper bound, because the interaction with the tip apex will pull the atom away from the surface and thus reduce the magnitude of lateral interactions between the surface and the atom [2]. Also temperature will assist to cross the barrier. Moreover, since there is no direct way to determine the chemical composition of the tip apex, it is possible that tungsten atoms are located at the tip apex. These would exert significantly higher binding forces than copper atoms [18].

One technical problem which has to be solved for manipulating native substrate atoms is to prepare a tip which is stable enough to resist the high attractive forces during the extraction of single atoms from high coordinated substrate sites; up to now this was simply done by usual trial and error techniques. Having succeeded in preparing a tip capable of a certain manipulation procedure, it can be repeated reliably many times. This leads to the possibility that extended parts of the substrate can be restructured in an atom by atom way. We demonstrate this in Fig. 4, in which more than 30 atoms were removed from kink sites using processes *d* and *a* of Fig. 1, so that a rectangular area on the terrace below is laid open. Such operations will be of importance in cases in which subsurface defects should be identified, removed, or deliberately created.

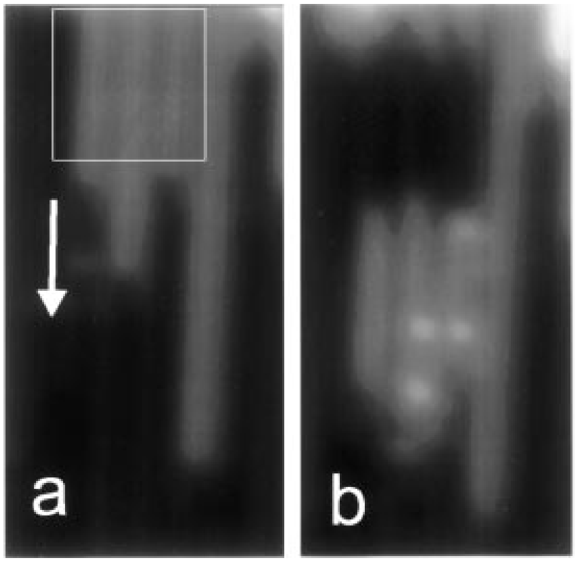

FIG. 4. Extended substrate restructuring employing processes *d* and *a* in Fig. 1. From the area indicated by the square in (a) more than 30 atoms of the upper terrace are displaced to open up a rectangular area on the lower terrace as shown in (b). The sample bias voltage was 47 mV. The current used for manipulation was 130 nA and for imaging 1.35 nA. Notice that in (b) a few atoms have been transferred on top of the upper terrace using process *e* in Fig. 1.

We expect that the above surface restructuring should be similarly applicable on the large number of Cu surfaces containing surface atoms with seven nearest neighbors. (The Cu(110) and Cu(113) surfaces might be borderline cases.) On the Cu(100) and Cu(111), which have surface atoms with eight and nine nearest neighbors, respectively, probably much higher forces will be necessary, so that eventually repulsive forces will have to be applied to extract atoms from regions inside extended terraces. It will, however, again be possible to extract atoms from kink sites and defect steps.

In summary, we have shown to be able to remove single native substrate atoms in a controlled manner from differently coordinated sites of the substrate by using a lateral STM manipulation technique. Apart from using the substrate atoms—and the corresponding vacancies—to build prototypic nanostructures, the new operations will be of importance in gathering information about subsurface defects. Since atoms may be moved into vacancy sites, with foreign species atom by atom surface alloying can become possible. Finally, one might speculate that structures deliberately built up with foreign species can be covered (and protected) with layers of native atoms.

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