New Mechanism for Single Atom Manipulation

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Scanning tunneling microscope (STM) investigations of the step roughening of Ag(110) have shown that the STM tip extracts atoms from otherwise stable steps even at typical imaging conditions. Detailed analyses of single STM scans reveal that none of the so far known lateral manipulation mechanisms (pushing, pulling, sliding) account for the observed atom extraction. The Ag atoms rather follow the energetically favorable path of a tip induced *exchange process*, similar to the concerted motion proposed previously for the diffusion on fcc(110) surfaces including a metastable and thus experimentally detectable *dumbbell transition state*.

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The fascinating capability of manipulating single atoms and molecules with atomic scale precision makes the scanning tunneling microscope (STM) a powerful tool of nanotechnology [1–3]. Two different techniques have been developed for nanostructuring by sophisticated low temperature STM experiments: (i) vertical manipulation, where the species are picked up by the STM tip at one place and deposited at another [4,5], and (ii) lateral manipulation, where the species remain at the surface during the displacement; analysis of single STM scans recorded during the lateral manipulation revealed the different mechanisms of pushing, pulling and sliding [6]. Meyer *et al.* recently succeeded in removing single atoms even from the step edges of Cu(211) [7]. The latter finding indeed is astonishing as the manipulated atoms in total loose two nearest neighbor bonds, broken just with the aid of a still distant STM tip. Since steps represent an abundant supply of native atoms at surfaces, understanding of this particular manipulation mechanism, i.e., of the controlled extraction of step atoms, is an essential prerequisite for the routine buildup of artificial nanostructures.

Recent STM investigations of step roughening at elevated temperatures underline the important role of tip/surface interaction even at typical imaging conditions [8,9]. On Ag(110) single atoms are extracted by the tip from otherwise stable steps running parallel to the close packed rows (Fig. 1) even at tunneling resistances in the GΩ range [10]. Here we present a thorough analysis of single STM scans observed on Ag(110) during the tip induced step roughening. "Snapshots" of metastable transition states disclose the mechanistic details of a new variant of lateral manipulation, where atoms follow the energetically favorable path of a tip-assisted exchange process—similar to the atom exchange mechanism proposed for diffusion on fcc(110) surfaces [11–14].

The experiments were performed in an ultrahigh vacuum chamber (base pressure $<1 \times 10^{-10}$ hPa) equipped with a home-built variable temperature STM [15], low energy electron diffraction and the usual facilities for sample preparation. The Ag(110) sample was prepared by

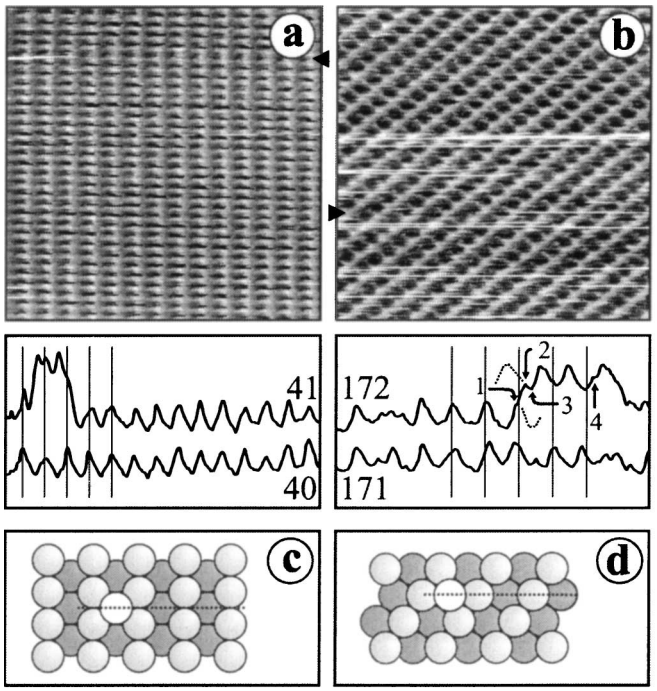

FIG. 1. (a), (b) 5.7×5.7 nm^2 atomically resolved STM images of the *same* surface area of Ag(110) at 340 ± 10 K with the fast scanning direction orthogonal (a) and diagonal (b) to the close packed rows; tip voltage $U_T = 725$ mV, $I_T = 1.0$ nA, 256×256 data points; scanning time per line: 0.11 s in (a) and 0.05 s in (b); notice the raised single scans with numbers 41 and 172, where the tip has trapped and pulls along diffusing adatoms. (c), (d) Sphere models to illustrate atom pulling via an exchange mechanism in orthogonal (c) and diagonal (d) scans (for details see text); we remark that the respective experimental single scans may deviate slightly from the path given by the dashed lines as indicated, e.g., by the considerable corrugation of the terrace atoms in scan 41.

repeated cycles of Ne ion bombardment and annealing at 600 K. The STM images were taken in the constant current mode with chemically etched tungsten tips; they were scanned from top to bottom with the fast scanning direction running from left to right, but at different angles with respect to the close packed rows of Ag(110).

The important contribution of an exchange mechanism for diffusion and tip-assisted movement of atoms on Ag(110) can be conceived already from a closer look onto atomically resolved images of interior regions of flat terraces (e.g., Fig. 1). Single scans occasionally are raised by the height of about one monostep indicating that adatoms are imaged by the STM tip (bright stripes in Fig. 1). The corrugation of the lifted scans is shifted by half a lattice period as compared with the underlying terrace (compare subsequent line scans of Fig. 1), thus confirming that indeed *adatoms* are detected at the fourfold hollow sites of the (110) terraces. We remark that atoms intermediately adsorbed at the tip itself would also give rise to lifted scans but *in phase* with the terrace periodicity. Comparison of the two top views of Fig. 1 reveals that the length of the bright stripes depends significantly on the scanning direction, extending typically only one lattice unit, when the fast scanning direction is orthogonal to the close packed rows (Fig. 1a), i.e., along [001], and several lattice units for diagonal scans (Fig. 1b). As in both top views, the *same* surface area is imaged, i.e., guaranteeing identical adatom density, these results point to a participation of the tip. According to previous experimental [11] and theoretical [12–14] studies, diffusion across the close packed rows of fcc(110) surfaces preferentially proceeds by an energetically favorable atomic exchange mechanism. Here the diffusing adatom replaces a terrace atom which itself becomes an adatom in one of the two diagonally opposite fourfold hollow sites (compare Fig. 2 while ignoring yellow atoms of upper terrace).

According to theory [12–14] the atom exchange proceeds via a so-called dumbbell configuration, in which the two involved atoms are placed symmetrically in hcp sites along the [001] direction (compare sphere model of Fig. 2b). A detailed analysis of STM images of atomically resolved terraces reveals that on Ag(110) the scanning tip is capable—as precursor of the dumbbell structure—to pull atoms from stable fcc to hcp sites. Figure 3 displays line scans along [001] from "adatom-free" terrace regions of Fig. 4d together with sphere models in side and top view representation; the vertical lines indicate the positions of the topmost close packed rows. Whereas the majority of the lattice sites is imaged without "perturbations" as in Fig. 3a, in about 10% of the scans the corrugation is superposed by small but well resolved peaks (Figs. 3c and 3c). At first sight, these peaks appear to be just noise. A closer look, however, reveals that nearly all of these peaks are located at the flanks of the rows, i.e., directly above the hcp sites, not on top of or in between the rows. It is noteworthy that the position of the peaks can be determined exactly by comparison with the neighboring scans. From the fact that only two distinct peak positions are generally observed, electronic and mechanical perturbations or tip instabilities can be

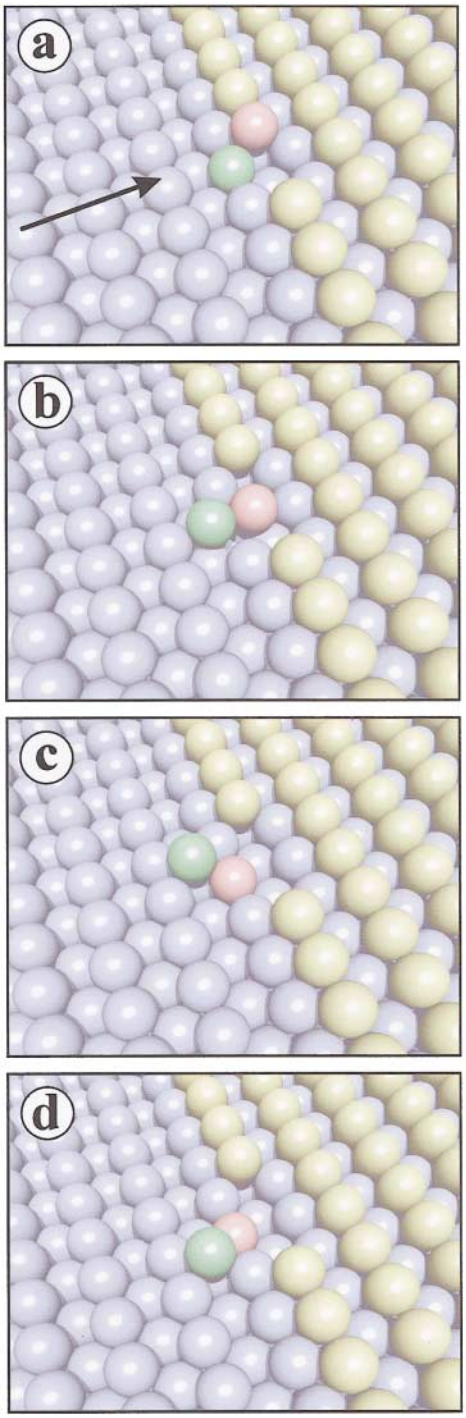

FIG. 2 (color). Sphere model of the Ag(110) surface with one monostep illustrating the tip-assisted exchange mechanism at step edges (fast scanning direction is indicated by the arrow): (a) initial configuration with one step edge atom missing (see text); (b) metastable dumbbell configuration (compare Fig. 4b); (c), (d) possible configurations after the extraction of one atom from the step edge. Notice: For illustration of the exchange mechanism for adatom diffusion on (110) terraces, regard the red atom as adatom and ignore the rest of the upper terrace (yellow).

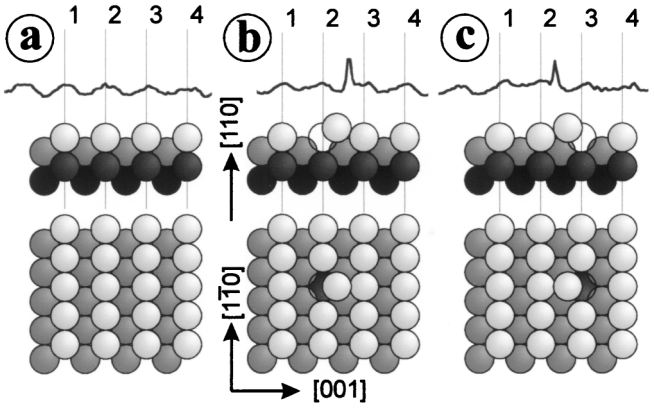

FIG. 3. Line-scan sections from the Ag(110) terraces of Fig. 4d with sphere models in side and top view representation: (a) undisturbed terrace (section of scan 317); (b), (c) atomic jumps from fcc to hcp sites (sections of scan 494 and 400, respectively).

excluded as explanations, since they should give rise to randomly distributed noise. Obviously, the peaks are the result of real, though only temporary, atomic rearrangements at the surface, namely, when the tip pulls Ag atoms to the hcp sites lying on the right and left side of the rows. We explain this important process in more detail by means of the line scan of Fig. 3b. Coming from the left the tip follows the contours of rows 1 and 2. While moving on to row 3, the just imaged Ag atom of row 2—attracted by the tip—suddenly jumps to the respective hcp site (compare sphere model of Fig. 3b). Consequently, the feedback loop of the STM retracts the tip (as fast as possible) causing the stabilizing attractive force to diminish. As the Ag atom returns to its (stable) original site, the tip is approached again and the normal scanning continues. In general, atomic motions are very fast compared with the velocity of the feedback loop.

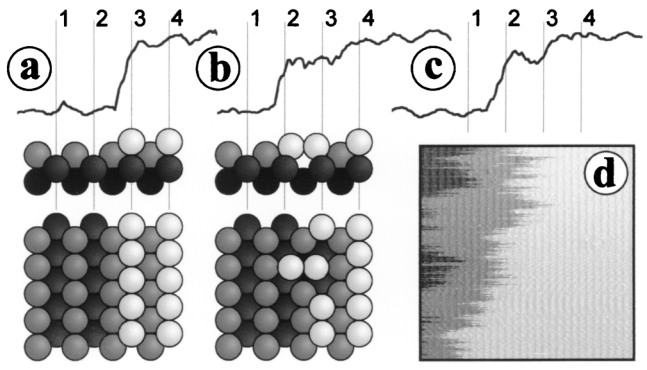

FIG. 4. (a)–(c) Line-scan sections from the step edges of (d) with sphere models in side and top view representation: (a) undisturbed step edge (scan 160); (b) dumbbell configuration (scan 319; compare Fig. 2b); (c) decay of the dumbbell configuration (scan 508). (d) 12×12 nm^2 STM image showing steps of Ag(110) at 310 ± 5 K; tip voltage $U_T = -153$ mV, $I_T = 0.5$ nA, 512×512 data points; scanning time per line 0.33 s, per image 338 s.

Therefore an analogous process is observed also in the opposite direction (Fig. 3c). In this case, the Ag atom of row 3 jumps towards the approaching tip into the respective hcp site.

After analyzing the tip induced processes on the (110) terraces, we now can turn to the mechanism for the tip-assisted extraction of atoms from step edges. Recently we have demonstrated that straight $[1\bar{1}0]$ steps of Ag(110) are completely stable in the absence of an STM tip but roughen upon scanning, because Ag atoms are pulled out [10]. The steps usually appear fringy in STM images (e.g., Fig. 4d) due to the rapid movement of the generated kinks [16]. Figures 4a–4c display three different line scans taken from Fig. 4d, which are observed with nearly equal probability (20%–30%) at the fringy step edges of Ag(110). The line scan of Fig. 4a shows the expected contour of a step edge: Approaching from the left the tip images small undulations of the close packed rows; at the step edge the tip is pulled back and finally the upper terrace is imaged. The maximum slope at the step edge is determined by the preset velocity of the STM feedback loop as well as the data point density. The scan of Fig. 4b shows a different behavior. An additional broad shoulder is detected with a height of approximately $2/3$ of a monostep. Also here tip effects can be excluded as a possible explanation. On the one hand, similar scans are obtained with completely different STM tips, exchanged as whole or microscopically modified *in situ*. On the other hand, the different scans are obtained from one STM image such as Fig. 4d, with no hint that the tip has changed while taking the image. Of course, all other parameters, such as the tunneling current and voltage, temperature, and the settings of the feedback loop, are constant during taking an image; therefore any dependence on these parameters can be excluded also. Thus, the shape of the scans indeed reflects structural information.

Assuming that the tip—analogous to the findings on the terraces—pulls atoms into the hcp sites lying close to the step edges leads to the scenario illustrated in Fig. 2; we consider here a geometry, where one atom in the step edge is missing (see discussion below): As usual, the tip approaches from the left. When it reaches the close packed row in front of the step, due to the attractive tip force a Ag atom jumps from its fcc site to the hcp site on its left. At the same time—at least on the time scale of the tip motion—a step edge atom moves into the neighboring hcp site, thus forming the symmetric arrangement of two atoms in hcp sites, i.e., the dumbbell configuration illustrated in Fig. 2b. The tip retracts to scan the dumbbell, which in accordance with the hard sphere model exhibits a height of $2/3$ of a monostep. Eventually the tip continues scanning on the upper terrace.

The good agreement of the experimental values of both the height and the lateral position of the dumbbell (Fig. 4b) with that of a hard sphere model (Fig. 2b) provides striking evidence that we indeed succeeded to detect the metastable intermediate state of the exchange mechanism. The

dumbbell configuration was predicted in previous studies by the embedded atom method [12], corrected effective medium theory [14], and molecular dynamics [17] for diffusion perpendicular to the close packed rows via an atomic exchange mechanism on various fcc(110) surfaces (Ni, Cu, Ag, Pd, etc.). Since our recent study [10] reveals that $[1\bar{1}0]$ step edges of Ag(110) are stable without scanning, the intermediate state observed here must be induced and stabilized by the tip. The dumbbell may decay either by returning to the original configuration (Fig. 2a) or to a state with an atom removed from the step edge and an adatom appearing in front of the step edge via the tip-assisted exchange mechanism (Figs. 2c or 2d). The line scan of Fig. 4c indicates the decay of the dumbbell while the tip is still on top of it. We remark that the discussed geometry with a vacancy in the step edge is quite common on fluctuating step edges (see Ref. [10]). The tip-assisted exchange mechanism may be possible also in the absence of a vacancy, though with lower probability, because two bonds have to be broken instead of one. However, in this case the identification of the more complex transition state by STM scans is not unambiguous.

Finally, we return to the raised single scan sections of Fig. 1 in order to discuss the tip-assisted adatom diffusion on the terraces in more detail. Analogous to the findings discussed above, also the apparent noise detected in the ascending section of the line scans can be interpreted in physical terms. A closer view to scan 172 (and similar scans) reveals that the two perturbations, marked by 1 and 2, actually indicate the abrupt change of the scan profile recorded typically on the terrace to that of an adatom (see dashed lines). In fact, when an adatom approaches from behind while the tip is scanning position 1, it retracts to position 2 to reproduce the corrugation of a neighboring adatom as usual. At position 3 an atom is imaged under the tip, which—in accordance with the discussion above—appeared in the fourfold hollow site via rapid atom exchange. Upon further scanning, tip-assisted diffusion by atom exchange is continued. The small spike detected at the ascent of scan 41 of Fig. 1a may indicate that also in the orthogonal scans the tip-assisted diffusion proceeds by an exchange mechanism. However, whereas in diagonal scans the lines of optimum pulling and trapping (on top of the adatom) are identical, they are shifted by half of a lattice distance in orthogonal scans (compare sphere models of Fig. 1). Therefore the tip-assisted exchange mechanism seems to be less effective in orthogonal scans. The small shoulder (4) detected at the last protrusion of diagonal scan 172 even indicates the intermediate formation of a dumbbell configuration, although the tip movement is not directly passing the hcp site.

In conclusion, by detailed analysis of single scans recorded on the terraces as well as on the step edges of Ag(110), we are able to provide convincing evidence for the existence of the metastable dumbbell intermediate state, thus revealing a tip-assisted exchange mechanism for the extraction of atoms from otherwise stable step edges as well as for adatom diffusion on the terraces. Thus, we discovered a new mechanism for atomic manipulation which will play an important role in future substrate modification on an atomic scale. Further improvement of the manipulation efficiency by variation of the scanning orientation will be addressed in a future study.

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