Tip-Assisted Diffusion on Ag(110) in Scanning Tunneling Microscopy

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(Received 13 November 1995)

The influence of the tip in a scanning tunneling microscope on the atomic motion of Ag on Ag(110) is investigated at $T = 50$ and 295 K. At $T = 50$ K the tip can move single Ag atoms preferentially along $[1\bar{1}0]$ via an attractive interaction. At $T = 295$ K, the tip can displace monatomic steps over distances as large as several hundred Å. The structures thus created decay on a time scale of minutes. In contrast to prevailing assumptions significant tip-induced disturbances of the equilibrium shape of steps are observed even at sub-nA tunneling currents.

PACS numbers: 68.35.–p, 61.16.Ch, 68.55.Jk, 81.10.Aj

Imaging of atomic surface structures and processes has become common since the invention of the scanning tunneling microscope (STM) [1]. Simultaneously, engineering of artificial structures with nanometer or even atomic dimensions has become feasible in many laboratories [2–5]. Whether a structure is imaged or manipulated depends on its stability with respect to the extreme conditions which exist between sample and tip. In the tunneling gap the electric field strength approaches values which are sufficient to break atomic bonds and the current densities can exceed those of conventional electron beams by many orders of magnitude [6]. Fortunately, as experience has shown, many aspects of STM images can still be interpreted assuming that tip-induced disturbances are negligible. However, does this assumption still hold when the STM is used to study the atomic details of more susceptible phenomena such as diffusion or surface roughening?

In this Letter we address one aspect of this problem. In STM images of monatomic steps on Ag, Au, Cu, and Pb surfaces obtained at ambient or elevated temperatures successive scan lines show abrupt, random jumps ("frizziness") of what appears to be the step position [7–13]. This observation has been interpreted in terms of thermal diffusion or kink-creation processes at steps which are undersampled in time. From statistical analyses of the jumps activation energies have been inferred. Often, a possible influence of the tip was excluded or not discussed. On the other hand, from their STM images of Cu(111), Thibaudau and Cousty inferred that tip-surface interaction may play an active role in the appearance of steps [14]. Speller *et al.* [13] observed indications for tip effects on Pb at low tunneling resistances ($R_t = 8.3$ MΩ) and, therefore, did not fully exclude a contribution of tip-surface interactions to the frizziness at larger resistances.

Here, STM observations of atomic mobility on Ag(110) at cryogenic and ambient temperatures are reported. The principal results are as follows: at low temperatures, individual atoms can be controllably moved by the tip along $[1\bar{1}0]$ (i.e., through troughs between densely packed atomic rows), yet steps usually appear smooth. *At ambient temperatures, however, the STM tip can displace steps over distances as large as several hundred Å.* The nonequilibrium step shapes thus created decay on a time scale of minutes akin to three-dimensional profiles used to measure surface self-diffusion [15,16]. We find that on Ag(110) tip-assisted motion occurs even for large resistances ($R_t = 4$ GΩ) and, therefore, jeopardizes previous interpretations of the frizziness of steps.

The experiments were performed with a custom-built ultrahigh vacuum (UHV) STM operated at temperatures $T = 50$ and 295 K [17]. The Ag(110) surface was prepared by Ar ion bombardment and annealing cycles. Individual Ag atoms were obtained by extraction from step edges with the STM tip or by evaporation onto the Ag substrate at $T = 50$ K. Electrochemically etched W tips were prepared in UHV by heating and Ar ion bombardment. Similar results were obtained with freshly prepared tips and tips which had been used for several days. All STM images were acquired in the constant current mode and are displayed such that the scan lines (fast scan direction) are horizontal and scanning proceeds from the bottom to the top.

The result of a manipulation experiment performed at $T = 50$ K is shown in Fig. 1. Image 1(a) which was acquired with $i_t = 2$ nA shows a flat terrace on which the rectangular unit cell of Ag(110) is resolved. Three adatoms (1, 2, 3) are imaged as protrusions. In 1(b) the same area is imaged using $i_t = 53$ nA in the lower part and $i_t = 2$ nA at the top. This variation of i_t leads to an abrupt change of the apparent surface height which is visible in the upper part of the image. More importantly, the adatoms are displaced along $[1\bar{1}0]$ at high i_t. Atoms 1 and 2 are pulled by the tip until the current is finally decreased whereas atom 3 is displaced by ≈0.9 nm only. While being pulled the atoms are repeatedly imaged as small protrusions. The image of the underlying Ag terrace is essentially unchanged. Image 1(c) shows the final adatom configuration after the manipulation experiment.

To understand Fig. 1(b) one should recall that the present STM images were acquired by scanning the surface area line by line proceeding from the bottom to the top of the image. If one assumes that there is

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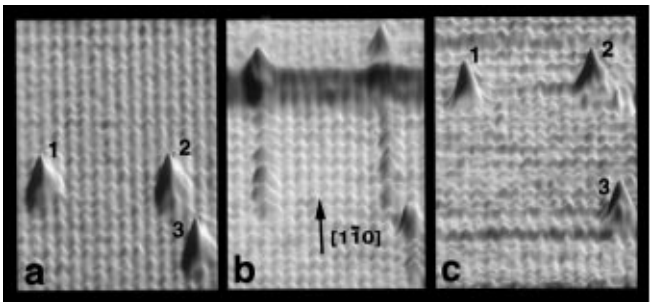

FIG. 1. Pseudo-three-dimensional images of a 6.3 nm × 6.0 nm area of a Ag(110) surface at $T = 50$ K. Image (a) was acquired with $i_t = 2$ nA and $V_t = -0.36$ V. It shows a terrace on which the Ag(110) unit cells are resolved. Three Ag adatoms $(1, 2, 3)$ are imaged as protrusions. In (b) the same area is scanned with $V_t = -0.02$ V using $i_t = 53$ nA in the lower part and $i_t = 2$ nA at the top. The variation of the i_t causes the abrupt change of the apparent surface height. More importantly, the adatoms are displaced along $[1\bar{1}0]$ at high i_t. While being pulled the adatoms are repeatedly imaged as small protrusions. Image (c) shows the final configuration after the manipulation experiment ($i_t = 2$ nA).

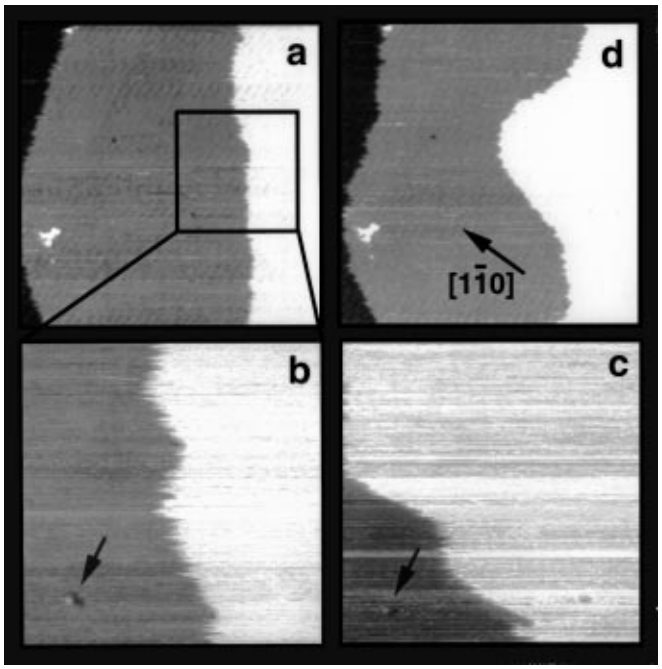

FIG. 2. (a) Gray-scale representation of a STM image of a $(160\ \text{nm})^2$ area of Ag(110) obtained at $T = 295$ K. Three terraces are separated by a curved (left) and a straight (right) monatomic step. (b) $(64\ \text{nm})^2$ closeup of the central part of (a) ($i_t = 0.1$ nA, $V_t = 0.37$ V). At the step edge frizziness is visible. (c) The same area as in (b) scanning at $i_t = 10$ nA. While the step position is hardly changed in the first few scan lines (bottom) it gradually shifts to the left as the scanning proceeds. A contamination spot marked by arrows in (b) and (c) serves as a reference point. Subsequently, image (d) was measured on approximately the same area as (a). A bell shaped protrusion has formed at the formerly straight step. In the vertical direction it exceeds the area scanned in (c).

an attractive interaction between the tip and the atom which at a distance of ≈3 Å is sufficiently strong to move an adatom along $[1\bar{1}0]$ but too weak to permit motion across atomic rows, one is led to the following interpretation. During the scan lines at the bottom of Fig. 1(b) the surface is imaged as in 1(a). When the tip passes horizontally one unit cell below an adatom it is pulled downwards by one unit cell [18]. The interaction of tip and adatoms is not sufficiently strong, however, to move the adatoms sideways. In the subsequent scans the adatoms are imaged repeatedly and pulled upwards along $[1\bar{1}0]$ in a series of jumps between hollow sites.

We have performed such experiments for various tunneling parameters in which atoms were displaced over many unit cells. Typically, the tip-induced motion occurs for MΩ tunneling resistances. In previous experiments performed at $T = 4$ K lower resistances were required to cause motion of Pt on Pt(111) and Fe on Cu(111) [3]. We attribute this difference most likely to thermal vibrations at $T = 50$ K in our experiment.

At $T = 50$ K tip-surface interactions at nA currents suffice to move single atoms. One would expect significant effects of the tip at even lower currents in experiments at ambient temperatures where thermal excitations promote atomic mobility. Figure 2(a) displays a representative image of monoatomic steps on Ag(110) measured at $T = 295$ K together with a more highly resolved image of the central region in Fig. 2(b). A rather straight step extends from the bottom to the top of the image. The apparent position of the step edge fluctuates strongly between the scan lines of the image as has been observed previously on various surfaces [7–13]. A clear change occurs when the current is increased to $i_t = 10$ nA [cf. Fig. 2(c)]. While the step position is hardly changed in the first few scan lines (bottom) it gradually shifts to the left as the scanning proceeds. At the top of the image the step edge has been displaced by ≈30 nm to the left. One minute later, Fig. 2(d) was measured on approximately the same area as Fig. 2(a) using a smaller current $i_t = 0.1$ nA again. A bell shaped protrusion has formed at the formerly straight step.

This experiment demonstrates that at $i_t = 10$ nA the scanning strongly modifies the step shape and causes an accumulation of material on the lower terrace. Therefore, the shape of steps on Ag(110) and, in particular, the atomic-scale variations between scan lines should not be interpreted in terms of diffusion alone. This calls the prevailing interpretation of frizziness into question. We note that the moderate currents used in the present experiments are sufficient to create protrusions of typical dimensions of 10–50 nm. The atomic details of mobility at steps may be affected at $i_t \ll 10$ nA although it may be more difficult to unambiguously identify these effects.

The protrusion formed in Fig. 2 represents a nonequilibrium shape of the monoatomic step which had been approximately straight prior to its modification. Therefore, a relaxation to its initial state is expected. Figure 3 shows four images selected from a time-lapse sequence of measurements. On a time scale of 20 min the artificial step profile decays until it finally is approximately straight again [Figs. 3(a)–3(d)]. We note in passing that the decay of artificial surface profiles has frequently been used to measure surface self-diffusion [16,19]. Using a phenomenological description developed by Mullins [15] we have performed a numerical evaluation of the observations of Fig. 3 which favors evaporation of atoms from the step onto the terrace with respect to diffusion along steps as the principal decay channel.

It is important to test whether the effect of the tip can be neglected at the low current ($i_t = 100$ pA) used for the imaging in Fig. 3. A closer look at the data from Fig. 2 reveals that on Ag(110) even these currents can be sufficient to provoke a measurable distortion of steps. Figure 4(a) shows a magnified view of the marked region in Fig. 2(a). The same area scanned at a 3 times higher data point density is displayed in Fig. 4(b). The arrows *R* mark the unchanged position of a contamination spot which is used as a reference to exclude thermal lateral drift [20]. The position of the step as observed in Fig. 4(a) is indicated as a dotted line in Fig. 4(b). At the bottom of the image the step positions from 4(a) and 4(b) coincide. During scanning a continuous shift of the step position to the left is observed. This finding is identical to the case of Fig. 2(c) and directly indicates tip-assisted motion. From an analysis of many such observations we exclude thermal step wandering as the underlying mechanism. The shift of the step position between Figs. 4(a) and 4(b) occurs despite the identical tunneling currents used owing to the different line densities (0.48 and 0.16 nm, respectively). We note that contaminants (arrow *C*) can affect the tip-assisted motion. Figure 4 represents the principal finding of this Letter: *Even at sub-nA currents the STM tip can significantly affect the atomic motion of Ag on Ag(110) at ambient temperature*.

Returning to the question of which mechanisms are involved in forming the protrusion in Fig. 2(d) we are confronted with an intriguing problem. The protrusion is comprised of $\approx 10^4$ atoms. Taking into account that it was created by recording Fig. 2(c), which consists of 400 scan lines, one finds that on average ≈ 25 atoms have been accumulated during each scan. It appears unlikely that the tip would extract such an amount of material. Moreover, in Fig. 2(c) a gradual shift of the step position is initially observed which contradicts such a hypothesis. We further exclude the possibility that the shift is predominantly due to material transfer between the tip and the sample. Such an effect is readily detected by monitoring the vertical tip position.

The experimental observations of Fig. 3 demonstrate that surface diffusion is active and thus needs to be considered in explaining the formation of the protrusion. We therefore tentatively propose the following scenario. At $T = 295$ K, the tip can extract a few atoms from the step which are pulled onto the lower terrace. Since the tip

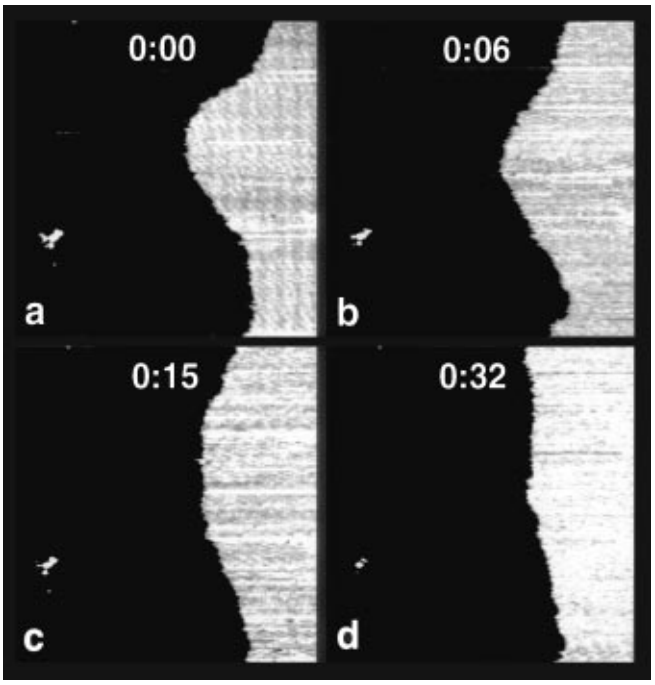

FIG. 3. Time-lapse sequence of images showing the evolution of the area of Fig. 2(d). The time when acquisition ended (in minutes) is noted on each image. (a) The step directly after manipulation in the central region of the image. A protrusion has been formed. (b)–(d) The decay of the protrusion. The lateral drift during acquisition of the images is negligible as apparent from the unchanged positions of contamination spots. $V_t = 0.37$ V, $i_t = 0.1$ nA.

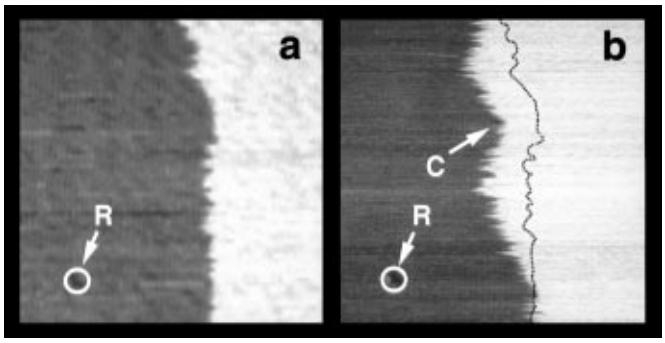

FIG. 4. (a) A magnified view of the marked region in Fig. 2(a). (b) is identical to Fig. 2(b). Owing to the higher data point density used (b) appears better resolved than (a). The arrows *R* mark a contaminant serving as a reference point. The position of the step from (a) is marked as a dotted line in (b). At the bottom the step positions in (a) and (b) coincide. During scanning a continuous shift of the step position to the left occurs indicating tip-assisted motion.

motion is slow (one unit cell per 0.4 ms) compared to the atomic diffusion on the terraces (mean square displacement ≈ 16 nm^2 in 0.4 ms [21]), diffusing atoms can condense at the atoms fixed by the tip and at the structure built up during the scan lines before. The attractive force of the tip may enhance this condensation. Thus the vacancies between these atoms and the step are filled by diffusing atoms from the neighboring area. This concept is consistent with several experimental facts. First, we find a gradual buildup of the protrusion. Next, since the number of surface atoms is conserved, vacancies should be generated nearby. This is indeed the case. In several experiments material is found to be lacking on both sides of the protrusion compared to the initial position of the step. Occasionally, holes are formed in the upper terrace. These observations are consistent with diffusion of the vacancies left by the atoms which were accumulated in the protrusion. Finally, in the experiment the formation of a protrusion is strongly affected by the distance between adjacent scan lines and by the scanning angle with respect to $[1\bar{1}0]$. At low temperatures these parameters were found to directly influence the ability to move adatoms.

In summary, at $T = 50$ K a STM tip can displace single Ag atoms on Ag(110), preferentially along $[1\bar{1}0]$. This motion occurs via an attractive interaction. At ambient temperatures, the tip can significantly disturb the equilibrium shape of steps even at sub-nA tunneling currents. This finding contrasts the previous assumption that STM imaging of diffusion processes is essentially nonperturbative. The step shapes thus created decay on a time scale of minutes.

It is a pleasure to thank E. L. Bullock, J. W. M. Frenken, J. Jacobsen, K. W. Jacobsen, A. Pimpinelli, P. Stoltze, and J. Villain for discussions. This work has been supported by the Swiss National Science Foundation.

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