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Oxygen-induced restructuring of Cu(19 19 1) studied by scanning tunneling microscopy

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Oxidation and the formation of a Cu-CuO stripe phase on the Cu(19 19 1) surface was investigated by means of STM. Since this surface is vicinal to the (110) orientation with step edges oriented perpendicular to the CuO stripes, it is especially well suited to study the changes in surface morphology induced by small amounts of oxygen. It is shown, that the tendency of the CuO stripes to grow lengthwise is strong enough to extend or displace certain terraces. Since this effect involves the transport of large amounts of Cu atoms, it strongly depends on surface mobility as shown by STM experiments carried out at different temperatures. On the clean Cu(19 19 1) surface a transition from multiple to single steps was observed after annealing at temperatures close to the roughening transition of Cu(110).

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I. INTRODUCTION

The adsorption of oxygen on Cu(110) and the formation of a Cu-CuO stripe phase have been the subject of numerous studies.[1–6] Molecular oxygen from the gas phase dissociates at the surface and combines with mobile Cu adatoms, which are released from step edges. Due to strong attractive interactions these Cu-O compounds agglomerate to form Cu-O chains oriented along the [001] direction. Upon further oxygen exposure these Cu-O chains assemble into islands of a reconstructed (2×1)O added row structure. At temperatures above 600 K, these islands arrange themselves in regular stripes oriented along the [001] direction and separated by bare Cu areas, forming a one-dimensional periodic grating.[3] Most of the studies concerning oxygen chemisorption on vicinal copper surfaces deal with (111) and (100) oriented vicinals.[7–10] In the present scanning tunneling microscopy (STM) study, a Cu(19 19 1) surface was chosen to examine the formation of the Cu-CuO stripe phase. It is vicinal to Cu(110) and consists of terraces with (110) orientation separated by (111) oriented steps running along the $[1\bar{1}0]$ direction. Due to the high step density and the perpendicular orientation between steps and CuO stripes, this system can provide new insights into the energetics and kinetics of the Cu-CuO stripe phase formation. Our STM measurements also provide complementary information on the process of oxygen-induced faceting of Cu(19 19 1), which has recently been examined by means of spot profile analysis low-energy electron diffraction (SPA-LEED).[11]

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure below 1×10^{-10} mbar. The vacuum chamber is equipped with an argon ion gun for sample preparation and an Omicron STM/AFM system. The STM images presented in this paper were recorded in constant current mode at a current of 1 nA and a tip bias voltage of 1 V. Sample cleanliness was checked by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) using a four grid LEED/AES system. We used a polished single-crystalline Cu(19 19 1) sample with a nominal miscut below 0.1°. The sample temperature was measured via a thermocouple attached to the manipulator in the vicinity of the sample transfer plate on which the crystal was mounted. The sample can be heated up to ~1000 K via resistive heating on the manipulator and up to 650 K after transfer to the STM. For the oxygen chemisorption experiments presented in this paper, the Cu(19 19 1) surface was prepared by argon ion sputtering with an ion energy of 900 eV and subsequent annealing at 900 K for 5 min.

III. RESULTS AND DISCUSSION

A. The clean Cu(19 19 1) surface

Figure 1(a) shows a typical STM image of a Cu(19 19 1) surface after argon ion sputtering and annealing at 950 K for 5 min. The numbers between neighboring (110) terraces indicate the height of the given step bunch in units of the monatomic step height $h=a/2=1.27$ Å. Very similar images are obtained for annealing temperatures between 500 and 950 K. Below 500 K, however, the order along the $[1\bar{1}0]$ direction, i.e., parallel to the step edges, is significantly reduced. By choosing an annealing temperature of 1000 K [Fig. 1(b)] or higher, a dramatic change in the surface morphology is observed. All step bunches break up and the surface exclusively exhibits monatomic steps and terraces with an average width of about 35 Å. Since the transition temperature lies between 950 and 1000 K, we suppose that it is related to the roughening transition, which occurs at around 1000 K for Cu(110).[12] The possible influence of segregating sulfur could be excluded by Auger electron spectroscopy monitoring the sulfur LMM transition at 153 eV during heating.

B. Oxygen chemisorption on Cu(19 19 1)

When the Cu(19 19 1) surface is exposed to oxygen and subsequently annealed at 650 K for 5 min, the increased mobility of the surface atoms at elevated temperatures enables two different processes that allow the Cu-O compounds to implement an energetically favored structure. First, they arrange themselves in regularly spaced stripes of elongated Cu-O chains on the (110) oriented parts of the surface as

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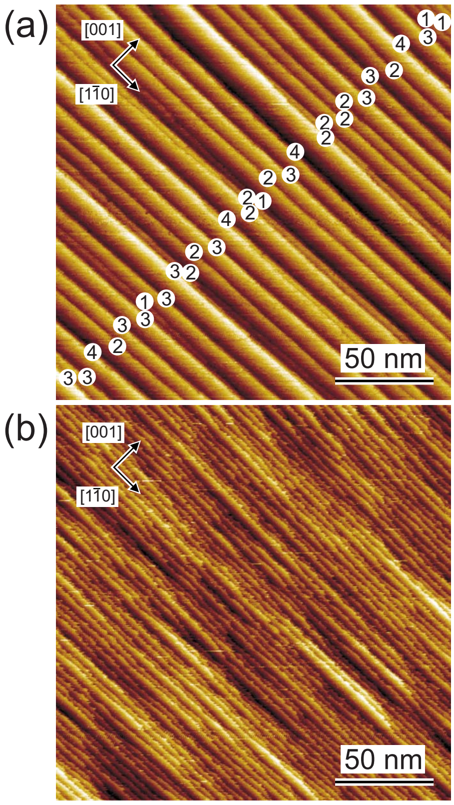

FIG. 1. (Color online) STM images of a 200 × 200 nm^2 area of the clean Cu(19 19 1) surface after argon ion sputtering and annealing at 950 K (a) and 1000 K (b) for 5 min. Numbers between neighboring (110) terraces in (a) indicate the height of the given step bunch in units of the monatomic step height $h=a/2=1.27$ Å.

reported by Kern *et al.*[3] Second, the tendency of the CuO stripes to grow lengthwise (perpendicular to the step edges) leads to a broadening of certain (110) terraces while, in order to maintain the macroscopic orientation of the vicinal surface, those in between shrink. The result is a faceted surface as shown in Fig. 2, where all the chemisorbed oxygen is gathered on the large (110) terraces, forming a local Cu-CuO stripe phase. Here, the sample was exposed to 1 L (1 L$=1\times10^{-6}$ torr·s) of oxygen at 300 K and subsequently annealed at 650 K for 5 min. Figure 3 shows typical cross sections along the [001] (a) and the [1$\bar{1}$0] direction (b) taken from the STM image in Fig. 2 (positions indicated by black lines). The periodicity of the stripe phase is about 70 Å [Fig. 3(b)], which is in good agreement with SPA-LEED measurements under similar conditions.[11] The profile in Fig. 3(a) has been tilted to make the (110) terraces appear horizontal. The dashed line indicates the nominal slope of 2.1° of the original (19 19 1) surface. It clearly shows that the slope of the facet between the large (110) plateaus is steeper at the edges whereas in the center, the original (19 19 1) slope is almost preserved. This underlines the role of the chemisorbed oxygen as the driving force for faceting. In order for the CuO stripes to extend along the [001] direction, certain (110) terraces are broadened by removing copper atoms from the neighboring upper terraces and adding them to the lower ones at the other side. Since this process involves the transport of large amounts of Cu atoms, it strongly depends on surface mobility and, therefore, on temperature. Figure 4 shows the distribution of the widths of the (110) facets (along the [001] direction) extracted from STM line scans. The Cu(19 19 1) surface was exposed to 1 L of oxygen at

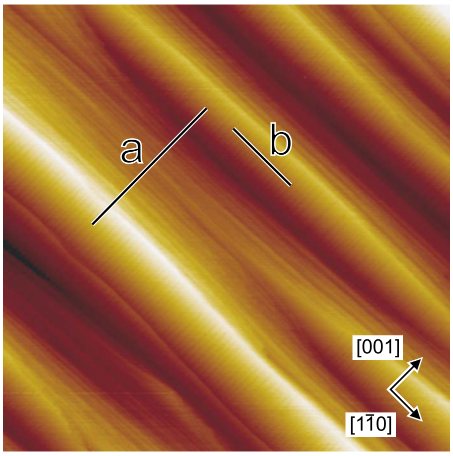

FIG. 2. (Color online) STM image (500 × 500 nm^2) of a Cu(19 19 1) surface after exposure to 1 L of oxygen at room temperature and subsequent annealing at 650 K. The solid lines indicate the positions of the height profiles shown in Fig. 3. Both ends of profile (a) are located on (110) terraces.

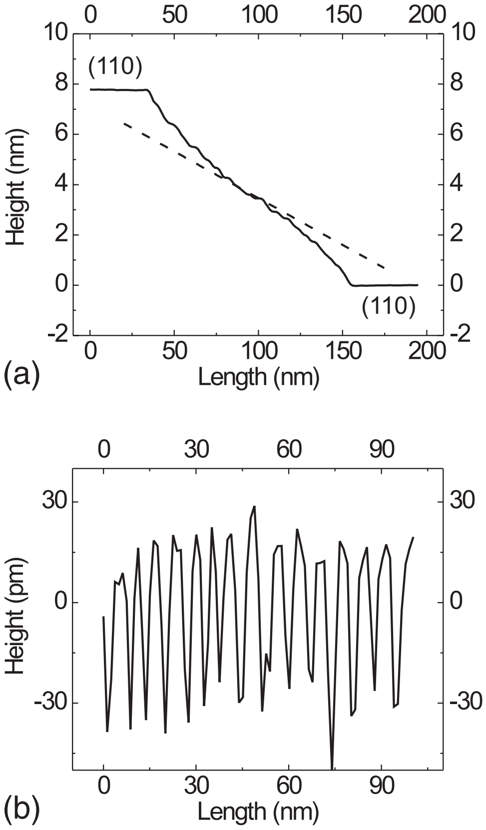

FIG. 3. Height profiles taken from the STM image in Fig. 2 along the [001] (a) and [1$\bar{1}$0] direction (b). (110) terraces appear horizontal. The dashed line in (a) indicates the macroscopic orientation of 2.1° of the original Cu(19 19 1) surface.

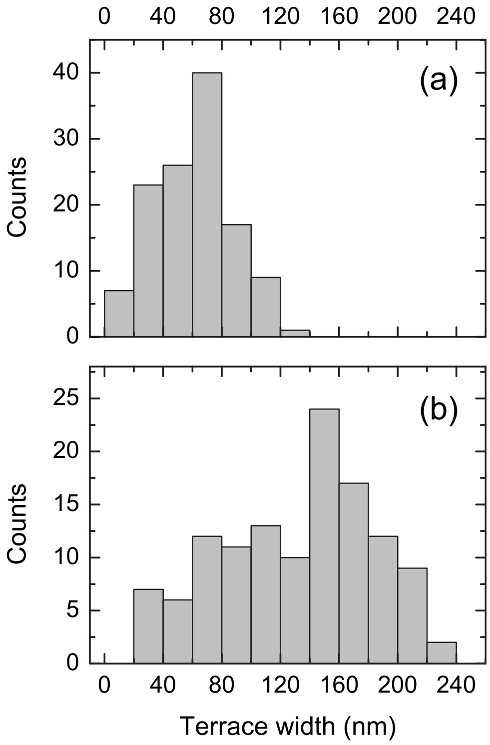

FIG. 4. Distribution of the widths of the (110) facets (along the [001] direction) extracted from STM line scans after exposure of the Cu(19 19 1) surface to 1 L of oxygen at 650 K (a) and subsequent annealing at 900 K (b).

650 K (a) and subsequently annealed at 900 K (b). The data clearly demonstrate that higher temperatures lead to broader (110) facets, driven by the tendency of the CuO stripes to grow lengthwise and promoted by the higher surface mobility. As revealed by SPA-LEED measurements,[11] a similar broadening can also be induced by increasing the amount of chemisorbed oxygen at a constant annealing temperature of 650 K, resulting in the coexistence of (110) and (111) facets for oxygen coverages close to saturation.

To gain more insight into the faceting process, the chemisorption of oxygen on Cu(19 19 1) was monitored at an atomic level for different temperatures. Figure 5(a) shows a typical STM image of the clean Cu(19 19 1) surface recorded at 300 K after argon ion sputtering and subsequent annealing at 900 K. Again, the numbers between neighboring (110) terraces indicate the height of the corresponding step bunch. Figure 5(b) shows the same section of the surface after exposure to about 3 L of oxygen. During the whole experiment the sample temperature was kept constant at 300 K. Therefore, thermal drift was low and defects on the surface were used to identify the exact scanning position before and after adsorption. A comparison of Figs. 5(a) and 5(b) reveals that the widths of the (110) terraces are essentially preserved. The changes in the shape of the step edges can be explained by the removal of Cu atoms from the upper step edges as required for the creation of the Cu-O compounds during the chemisorption process. The islands formed by these compounds (appearing dark compared to the bare Cu areas on the same terrace) exhibit a (2×1) superstructure[3] and show the tendency to extend along the [001] direction [see inset in Fig. 5(b)]. Still, the mobility is not high enough to form straight stripes and there is no long range ordering between the stripes along the $[1\bar{1}0]$ direction.

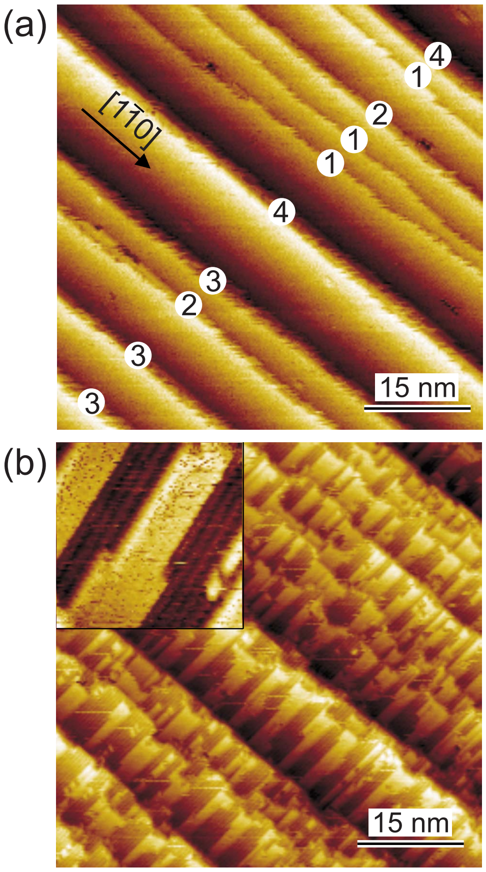

FIG. 5. (Color online) STM images of the same 60×60 nm^2 area on the Cu(19 19 1) surface before (a) and after (b) exposure to 3 L of oxygen at 300 K. The numbers between neighboring (110) terraces indicate the height of the given step bunch in units of the monatomic step height. The inset in Fig. 5(b) is a zoom-in on the partially ordered Cu-CuO stripe phase on a large (110) terrace (10×10 nm^2).

In Fig. 6 the results of a similar experiment carried out at 400 K are shown. Again, both STM images are taken at the same location and the numbers on the step bunches indicate their height in monatomic step units. Additionally, corresponding terraces are labeled with the same letter in both images. Due to the long time that was necessary to reach thermal equilibrium within the STM at this elevated sample temperature, the surface [Fig. 6(a)] already shows some contamination from the residual gas before oxygen exposure, as for instance on terraces C and F, which seem to act as nucleation centers for CuO compounds.

The STM images in Figs. 5 and 6 were recorded under the same tunneling conditions in constant current mode, and the higher mobility of the Cu atoms at 400 K can already be seen by the fringes at the step edges, which are clearly more pronounced at 400 K [Fig. 6(a)] than at 300 K [Fig. 5(a)]. The fringes result from Cu atoms which are released from the step edge and shifted by the STM tip along the fast scanning direction.[13] The effect of the increased mobility on the evo-

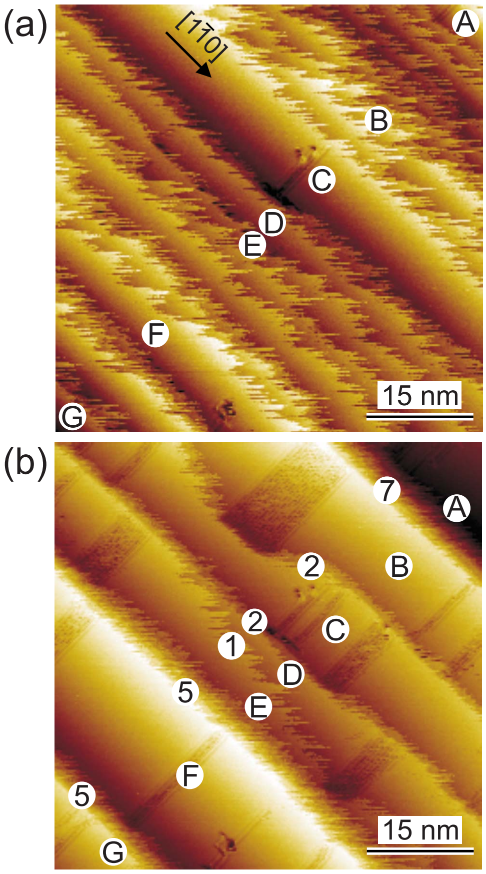

FIG. 6. (Color online) STM images of the same 60×60 nm^2 area on the Cu(19 19 1) surface before (a) and during (b) exposure at constant oxygen pressure of 7×10^{-9} mbar at 400 K. The oxygen exposure in (b) increases from the bottom to the top of the image, starting with 0.2 L and reaching 0.5 L. Numbers between neighboring (110) terraces indicate the height of the given step bunch in units of the monatomic step height. Corresponding terraces are labeled with the same letter in both images.

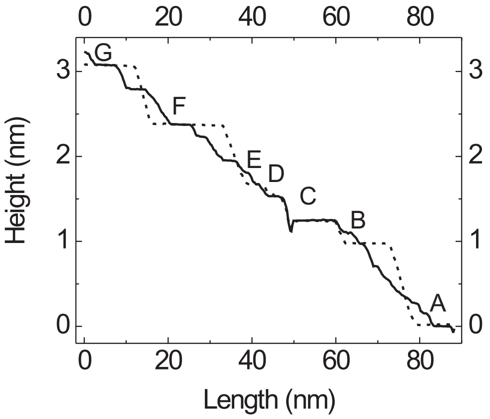

FIG. 7. Height profiles taken from the STM images before (solid line) and during (dotted line) exposure to oxygen [Figs. 6(a) and 6(b), respectively] corresponding to the diagonal reaching from the lower left to the upper right corner of the scan area. Prevailing terraces are labeled by letters A to G as in Fig. 6.

lution of the surface morphology upon oxygen chemisorption is obvious in Fig. 6(b). The image was recorded while the sample was exposed to a constant oxygen pressure of 7×10^{-9} mbar. Since the slow-scanning direction of the STM was upward, the exposure increases from the bottom to the top of the image, starting with 0.2 L and reaching 0.5 L. Obviously, the main features of the change in surface morphology are determined in the very first stage of oxygen chemisorption, i.e., before the upward scan shown in Fig. 6(b) was even started. Those terraces or parts of terraces, which first gather enough oxygen to form a stable Cu-O added row (again appearing dark as compared to bare Cu) are immediately broadened, driven by the tendency of the Cu-O rows to grow lengthwise along the [001] direction. Neighboring terraces that do not carry sufficient Cu-O compounds are displaced and shrink to minimum width, i.e., they are reduced to a part of the (111) oriented step bunch, reaching down or up to the next extended (110) terrace that could prevail. As Fig. 7 clearly shows, the broadening of the prevailing terraces occurs in both directions. The profiles shown in Fig. 7 were taken from the STM images of the surface before (solid line) and during (dotted line) exposure to oxygen [Figs. 6(a) and 6(b), respectively] and correspond to the diagonals reaching from the lower left to the upper right corners of the scan areas. The prevailing terraces are labeled by letters A to G in all three figures. Figure 7 illustrates the tremendous transport of Cu atoms induced by a very small amount of chemisorbed oxygen. For instance, the increased width of terrace F at the bottom of Fig. 6(b) indicates that the major changes in surface morphology are already completed at an oxygen exposure below 0.2 L. The fact that terraces C and F prevail upon oxygen chemisorption might be related to the pre-existing impurities on these terraces, favoring an early nucleation of CuO stripes. This would also suggest that upon oxygen chemisorption, such impurities rather lead to a broadening of a terrace than to pin step edges. Other types of impurities, however, such as the one appearing on the step separating terraces C and D in Fig. 6 and corresponding to the dip in Fig. 7 seem to be capable of pinning step edges. As revealed by STM measurements not shown here, in the absence of impurities CuO stripes may nucleate at the top, as well as at the bottom of the step edges.

The influence of temperature on the morphological changes upon oxygen exposure revealed in Figs. 5 and 6 is confirmed by statistical evaluations of STM line scans. In Fig. 8 we present the distributions of the step heights [measured perpendicular to the (110) orientation] and the terrace widths (along the [001] direction), respectively, for the clean Cu(19 19 1) surface (a), the surface after exposure to 2 L of oxygen at 300 K (b) and after subsequent annealing at 400 K (c). As mentioned above, the *average* width of the (110) terraces is essentially preserved upon oxygen chemisorption at 300 K. The large difference in the step heights and the concomitant changes in the terrace width *distribution* can be explained by the removal of Cu atoms from the upper step edges, which is required for the creation of the Cu-O compounds. The resulting local displacements of the step edges leads to the appearance of small terraces within a formerly narrow and straight step bunch, as can be seen in Fig. 5. Since the statistical analysis was based on line scans along the [001] direction, the removed Cu atoms appear as addi-

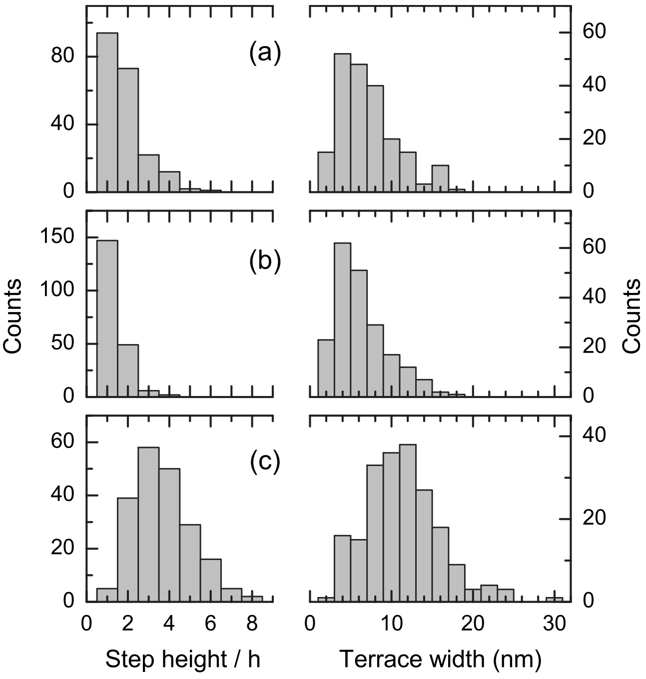

FIG. 8. Distributions of the step heights in units of the monatomic step height $h=a/2=1.27$ Å and the terrace widths (along the [001] direction) for the clean Cu(19 19 1) surface (a), the surface after exposure to 2 L of oxygen at 300 K (b), and after subsequent annealing at 400 K (c).

tional narrow terraces, whereas the width of larger terraces is slightly reduced. At the same time, the height of the original step bunch is reduced and additional monatomic steps appear. After annealing at 400 K, however, more drastic changes in the surface morphology are observed. As described above, certain terraces extend while others are reduced to a part of a step bunch, leading to a doubling of the average terrace width and a distinct increase in the average step height.

Finally we have studied the morphology of the Cu(19 19 1) surface after oxygen chemisorption at different temperatures and subsequent annealing. To this end, the surface was prepared by argon ion bombardment and subsequent annealing at 900 K, resulting in step bunches as shown in Fig. 1(a). Such a surface was exposed to the same amount of oxygen [1 L and 0.3 L in Figs. 9(a) and 9(b), respectively] either at 300 K (left) or at 650 K (right). In all cases the surface was subsequently annealed at 650 K for 5 min and the STM image was recorded after cooling down to room temperature. Contrary to intuition oxygen adsorption at higher temperature yields smaller structures (right panels in Fig. 9) as compared to adsorption at initially lower temperatures (left panels in Fig. 9). The remarkable difference in the widths and lengths of the prevailing (110) terraces is explained in the following: As shown in Figs. 5(a) and 5(b) the surface consists of terraces of different widths, which, when exposed to oxygen at 300 K, are more or less uniformly covered with a high density of Cu-O compounds. As revealed by STM images of the clean surface such as the one shown in Fig. 1(a) but over larger areas, the length of an average terrace along the $[1\bar{1}0]$ direction is at least 1 μm. When the temperature is raised, the mobility of the surface atoms is enhanced, and Cu-O chains form everywhere on the initially wider terraces, which thus extend in the [001] direction along their entire length and at the expense of the narrower terraces. Upon heating the sample up to 650 K these prevailing terraces are covered with a well-ordered Cu-CuO stripe phase. Thus, oxygen chemisorption at 300 K followed by annealing at 650 K gives rise to wide and elongated (110) terraces as seen in the left panels of Fig. 9. If, on the other hand, the surface mobility is already enhanced at the time of exposure, the Cu-O compounds can travel a large distance to form a stable Cu-O chain, which immediately broadens a certain terrace at one point, while at another position, the same terrace is narrowed due to the local extension of a neighboring terrace, which happens to have nucleated a Cu-O chain at this location. In fact, the finite stiffness of a step edge allows the complete constriction of a given (110) terrace if, at elevated adsorption temperature, the average spacing of the initial Cu-O chains along the $[1\bar{1}0]$ direction is sufficiently large. In this case, the (110) terraces will only prevail over a characteristic length related to this spacing. As the stiffness limits the step curvature, it also restricts the width in the perpendicular [001] direction of these terraces with finite length. As a result, after oxygen adsorption at 650 K, the surface exhibits lenticular (110) terraces, which are both shorter along the $[1\bar{1}0]$ direction and narrower in the [001] direction (right panels of Fig. 9) than after initial adsorption at 300 K (left panels of Fig. 9). In both cases (oxygen exposure at room temperature with subsequent annealing and exposure at el-

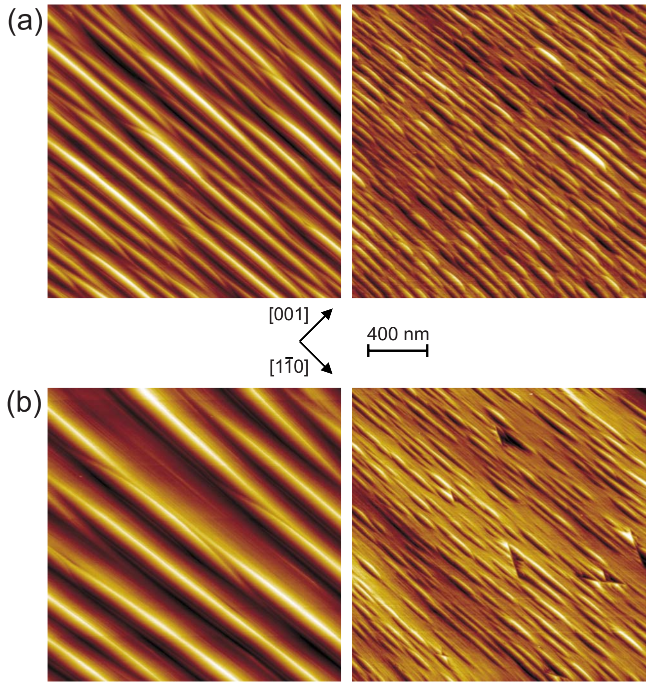

FIG. 9. (Color online) STM images over an area of 2×2 μm^2 of the Cu(19 19 1) surface exposed to the same amount of oxygen [1 L (a) and 0.3 L (b)] either at 300 K (left) or at 650 K (right). In all cases the surface was subsequently annealed at 650 K for 5 min. All images were recorded after cooling down to room temperature.

evated temperature), no significant amounts of oxygen could be found on the stepped facets between the large (110) plateaus. This is corroborated by a statistical analysis of the STM images suggesting that all the chemisorbed oxygen is indeed accumulated on the large (110) terraces.

IV. SUMMARY

We have shown that upon annealing close to the roughening transition temperature, a sputtered Cu(19 19 1) surface undergoes a transition from a multiple to a single-step morphology. The oxygen-induced restructuring was studied by STM for different temperatures, pointing out the influence of surface mobility on the morphological changes. At 300 K the terrace widths are essentially preserved, whereas at 400 K certain terraces are significantly broadened at the expense of neighboring ones due to the tendency of Cu-O chains to extend along the $[001]$ direction. At 650 K and above, oxygen chemisorption induces faceting of the surface, with all the oxygen being gathered on the large (110) terraces forming a local, well-ordered Cu-CuO stripe phase. The sample temperature during oxygen chemisorption also affects the terrace extension along the $[1\bar{1}0]$ direction, i.e., parallel to the step edges. In fact, oxygen exposure at 650 K leads to shorter (110) terraces than exposure at 300 K and subsequent annealing at 650 K.

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