Novel Mechanism for the Formation of Chemisorption Phases: The (2 × 1) O-Cu(110) "Added-Row" Reconstruction

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Scanning tunneling microscopy investigations on nucleation and growth of the (2×1)O-Cu(110) structure revealed that the new phase is formed by condensation of mobile chemisorbed O atoms with Cu adatoms evaporating from steps and diffusing across the terraces of the substrate surface. This process can be regarded as two-dimensional precipitation from a dilute mixed fluid into a solid phase rather than a solid-solid transformation. The resulting structure is more appropriately described to be of the "added-row" rather than of the "missing-row" type.

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With chemisorption systems, the strength of the bond between the surface and the adsorbate is frequently comparable to that between the substrate atoms. As a consequence, minimization of the total energy is often accompanied by displacements of atoms within the substrate lattice, which are either confined to position changes within the unit cell or are "true" reconstructions characterized by alterations of the density of substrate atoms. This latter process is associated with the migration of surface atoms. As an example we mention the CO-induced (1×2)→(1×1) transformation of Pt(110), which proceeds via homogeneous nucleation of holes in the topmost substrate layer, leading to an increase in the *local* density of surface atoms.[1] The same adsorbate causes the "hex"→(1×1) transformation on Pt(100) by "squeezing" atoms out of the topmost substrate layer into the next one, whereby the local density is reduced.[2] In general, these processes, leading to the formation of new chemisorption phases, are characterized by distortion of the initially perfect substrate lattice as the primary nucleation step and can be considered as two-dimensional solid-solid transformations. The present Letter will report on a novel mechanism, in which condensation of mobile substrate "adatoms" together with the equally mobile chemisorbed species leads to the formation of the new phase. This process represents a two-dimensional analog to the precipitation of a solid from a fluid mixed phase.

The conclusions to be reached will be based on observations, by means of scanning tunneling microscopy (STM), on the (2×1)O reconstruction process of a Cu(110) surface, induced by chemisorbed oxygen atoms. This system has been investigated quite extensively during the past two decades,[3] including a most recent STM study by Chua, Kuk, and Silverman.[4]

The experiments were performed with a pocket-size STM incorporated into a UHV system (base pressure about 10^{-8} Pa) as described elsewhere.[5] Oxygen exposures were performed by backfilling the chamber. The surface of the Cu(110) single crystal was cleaned by repeated Ar^+-ion sputtering and annealing cycles, until no impurities could be detected by Auger spectroscopy. Sharp LEED spots indicated a well ordered (1×1) lattice. High-resolution STM images exhibited large, flat terraces with parallel rows 3.6 Å apart from each other, reflecting the atomic rows running in the $[1\bar{1}0]$ direction. The corrugation within these rows, associated with the densely packed atoms (distance 2.5 Å), could, however, not be resolved.

Figure 1 shows a number of large-scale images from a series of STM measurements recorded during exposure to O_2 at 300 K. The grey scaling is such that in the upper panels of Figs. 1(a)-1(c) each grey level represents a single terrace, while, for higher display resolution, the terraces in the corresponding images of the

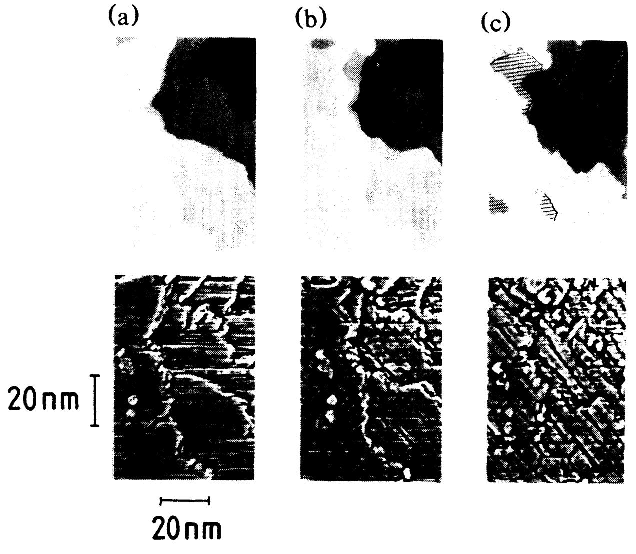

FIG. 1. Series of STM images taken after subsequent exposures to oxygen at 300 K. Upper panels: grey scaling such that the step-terrace topography can be visualized; lower panels: each terrace colored individually. (a) Clean surface. (b) Surface after total exposure of 6 L; dark areas (bottom) represent (2×1)O islands. (c) Surface after 10 L total exposure; hatched areas (top) represent regions where the topmost layer disappeared if compared with the clean surface in (a).

lower panels are colored in individual grey scales. Figure 1(a) shows the clean surface, which exhibits several terraces, separated by monatomic steps. The terraces are rather irregular in shape, i.e., the steps do not exhibit any preferential crystallographic orientation, in contrast, e.g., to the mostly $[1\bar{1}0]$-oriented steps on the (1×2)-reconstructed Pt(110) and Au(110) surfaces.[6] Upon adsorption of small amounts of oxygen the LEED pattern shows the appearance of faint streaks between the substrate spots, in the [10] direction of the reciprocal space, indicating the formation of strongly anisotropic nuclei of the (2×1)O phase.[3] This conclusion is confirmed by the STM image in Fig. 1(b) (bottom), recorded after a nominal O_2 exposure of 6 L (1 L$=1.34\times10^{-4}$ Pa sec). It depicts (in agreement with observations made by Chua, Kuk, and Silverman[4]) the formation of islands of the new phase, whose dimensions in the [001] direction are much larger than those along $[1\bar{1}0]$, and which are uniformly distributed over the entire surface area imaged. The STM image in Fig. 1(c) (bottom), taken after a total O_2 exposure of 10 L, demonstrates that these islands grow preferentially in the [001] direction, while their width along $[1\bar{1}0]$ has increased only slightly. In addition, a few new islands were created.

The dark stripes representing the (2×1)O patches in Figs. 1(b) and 1(c) (bottom) might be considered as an indication that this chemisorbed phase is "ploughed" into the terraces of the substrate. However, in the present case the STM response does not simply reflect the topography of the surface (as assumed by Chua, Kuk, and Silverman[4]). The apparent "height" of the (2×1)O islands with respect to the surrounding bare substrate was found to depend strongly on the experimental parameters in the STM measurement, i.e., gap distance and bias voltage. This is demonstrated by Fig. 2 which reproduces a series of STM line scans taken in the $[1\bar{1}0]$ direction across a (2×1)O island at different bias voltages. Since the tunnel current was kept constant at 0.4 nA throughout the series, the distance between tip and clean surface also varies in these examples. This is presumably the main reason for the observed differences. While the (2×1)O island is imaged as a "hole" in the (1×1) surface, with an apparent depth of up to 0.4 Å for bias voltages of about −0.7 V, it appears as an elevation of up to 0.3 Å for bias voltages of about −1.3 V. Similar effects were observed when the tunnel current (and thus the gap distance) was varied at fixed bias voltages. It has to be concluded that the apparent height of the (2×1)O islands with respect to the surrounding (1×1) substrate is not governed by the surface topography, and hence the dark areas in Fig. 1 cannot simply be interpreted as holes in the terraces of the clean Cu(110) surface.

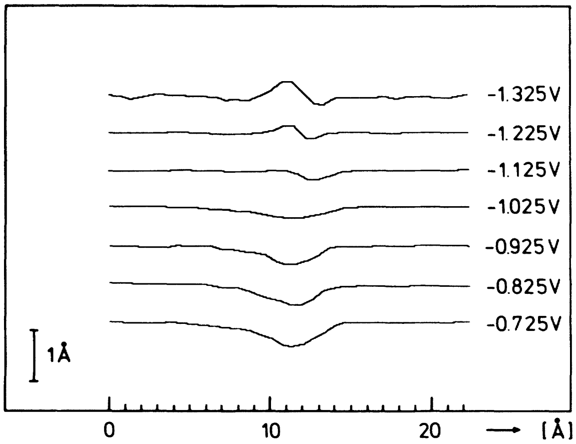

FIG. 2. Set of STM line scans taken at different bias voltages, in the $[1\bar{1}0]$ direction, over a (2×1)O island surrounded by a clean (1×1) substrate area. $I_t=0.4$ nA; V_t is as indicated; the slight asymmetry is due to an asymmetric tip.

It turns out that just the opposite is true. This becomes evident from inspection of the upper row of images in Fig. 1, which shows the distribution of terraces by a different grey level for each plateau. The hatched areas in Fig. 1(c) (top) represent areas where steps have retracted, i.e., Cu atoms from the topmost terrace disappeared and were used as material for the buildup of the (2×1)O islands on the adjacent terraces. This process is not necessarily confined to already existing steps, but may sometimes even take place in the middle of a previously flat terrace. The formation of a one-Cu-layer-deep hole in the lower left part of Fig. 1(c) (top) is one example. Quantitative evaluation of the topography of Figs. 1(a) and 1(c) revealed that the topmost layer has been removed from about 15% of the Cu(110) surface area, while the (2×1)O phase created simultaneously covers about 30% of the total surface. This result suggests that for the buildup of the (2×1)O phase additional Cu atoms are required, with a Cu adatom density of 0.5 monolayer in the (2×1)O islands. This will be supported by the actual structural model to be presented below. Obviously the oxygen-induced reconstruction of Cu(110) involves more than a mere displacement of substrate atoms and represents a "true" reconstruction, as indicated by the change in Cu density. The qualitative features of these observations were reproduced in a number of experiments. Frequently the process of Cu evaporation was found to take place only at a few regions, while the overall step-terrace topography was only slightly affected or not at all. The data also suggest that this process proceeds discontinuously, with significant local changes in the step-terrace topography only at certain times. Although in most cases material was removed from the steps, sometimes the terraces were also found to grow due to condensation of mobile Cu adatoms from the adjacent terrace. Finally, on (2×1)O-covered regions there was a general tendency to form linear steps, aligned in the [001] direction, instead of the rather irregular terrace configurations of the clean Cu(110) surface.

The results can be interpreted as follows: On the (1×1) surface at 300 K a finite concentration of mobile Cu adatoms is created by evaporation of terrace areas, mostly at the step edges. The individual adatoms are sufficiently mobile at this temperature so that they cannot be imaged by STM. They will, however, be trapped by coadsorbed oxygen atoms, due to strongly attractive Cu-O interactions. This attraction is strongest in the [001] direction, leading to a preferential growth of (2×1)O nuclei along this direction. With increasing size the resulting Cu-O adatom strings become stabilized and lose mobility. At 300 K nuclei of about six Cu atoms in length can be detected by STM. In addition, it was found that the nucleation probability is enhanced along steps on the clean Cu(110) surface with (local) [001] orientation.

Figure 3 shows an STM image exhibiting two elongated nuclei along [001] steps, two and three rows wide, respectively, together with a single-row nucleus on a flat terrace. In the latter the row does not form a straight line but consists of segments displaced by ca. 5 Å in the $[1\bar{1}0]$ direction from each other, equivalent to the periodicity of the (2×1)O phase in that direction. The abrupt changes and the fact that the morphology of this broken row changed from image to image indicate that this is a time effect. Entire sections of such a row are displaced in sudden events, between two STM scans, either spontaneously or induced by the tip. The segments, however, tended not to separate completely from each other in a subsequent jump but rather to return to the original straight configuration. Effects of this type were only observed with single rows of the (2×1)O phase on terraces, but not when such a row existed along a [001] step, or if two or more rows were adjacent to each other. This suggests the operation of additional, weaker attractive interactions between neighboring (2×1)O structural elements, as well as with adjacent [001] steps, which lead to a stabilization of the resulting (2×1)O nuclei in those cases. Closer inspection of the data in addition revealed that the (2×1)O rows always preferred the upper terrace at a [001]-step edge.

There is now overwhelming experimental evidence that the actual structure of the (2×1)O-Cu(110) phase is of the "missing-row" type as depicted in Fig. 4(c). This conclusion is based on recent evidence from ion scattering,[7,8] surface extended x-ray-absorption fine-structure spectroscopy,[9] photoelectron diffraction,[10] He diffraction,[11] and LEED (Ref. 12) data. In contrast, Chua, Kuk, and Silverman[4] favored a "buckled-row" model (exhibiting the same atomic density within the unit cell as the clean surface) on the basis of their STM data. In particular, they found (and this was confirmed in the present study) the corrugation along the (2×1)O rows, in the [001] direction, to exhibit maxima at positions which were in line with the $[1\bar{1}0]$ atomic rows on the surrounding clean (1×1) surface. This cannot be reconciled with any structure in which the O adatoms are adsorbed on long-bridge sites of the Cu surface atoms, neither with a missing-row structure nor with a chemisorption model such as the buckled-row structure, if the cor-

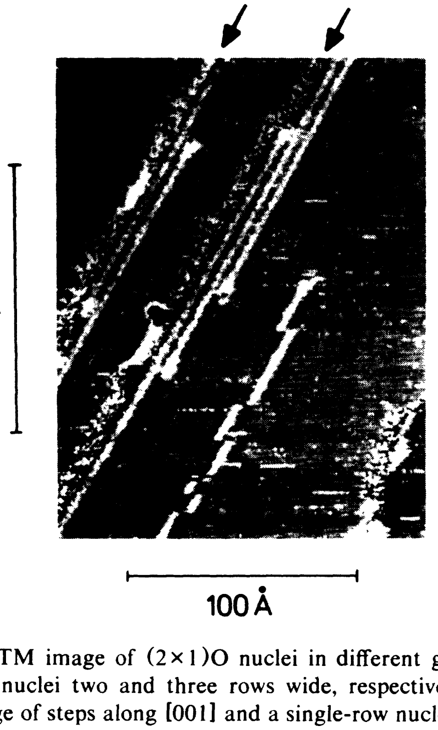

FIG. 3. STM image of (2×1)O nuclei in different growth phases: two nuclei two and three rows wide, respectively, at the upper edge of steps along [001] and a single-row nucleus on the flat terrace. Step edges are marked by arrows.

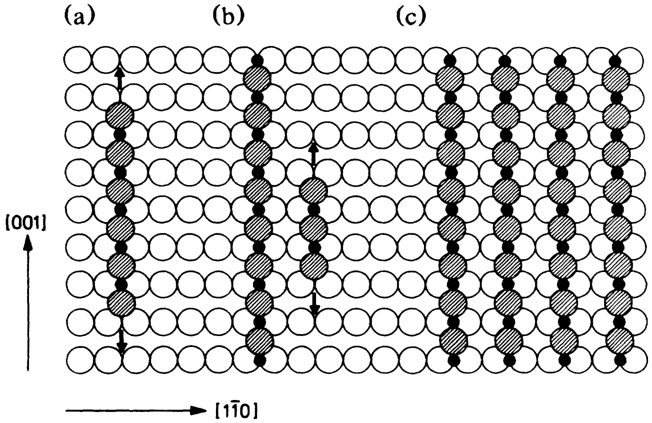

FIG. 4. Atomistic model of the different stages of (2×1)O formation. (a) Single string of Cu-O adatoms along [001] ("added row"); arrows indicate preferential growth direction. (b) Growth of a single-row (2×1)O island along [110]; nucleation of a neighbored added row. (c) Two-dimensional island of (2×1)O added-row phase, the structure being equivalent to the "missing-row" structure. Filled circles: O atoms; shaded circles: added-row Cu atoms on top of the substrate atoms (open circles).

rugation maxima are associated with oxygen adatoms. Therefore the above authors attributed these maxima to Cu atoms relaxed outward in the (2×1)O phase by 0.8 Å, where this quantity is concluded from the height difference to the surrounding (1×1) phase. The observed consumption of Cu atoms for the formation of (2×1)O islands is, however, incompatible with this model and leads instead to the prediction of an "added-row"-type structure for the (2×1)O islands as depicted in Fig. 4. In that case the oxygen atoms are in line with the Cu atoms forming the $[1\bar{1}0]$ rows of the bare surface and must be associated with the maxima along the (2×1)O rows seen with the STM. The additional rows of Cu atoms in the added-row structures shown in Fig. 4 rise even higher above the surrounding (1×1) phase than the relaxed Cu atoms in the buckled-row structure. However, as outlined before, the apparent height of the (2×1)O islands with respect to the (1×1) phase and even its sign depend strongly on the tunneling parameters, and hence the STM images cannot be used as a direct representation of the surface structure. Apparently under many conditions the adsorbed oxygen atoms lead to a decrease in the tunnel current in their direct neighborhood, counteracting the topographical effects, as it was found on other metal surfaces as well.[13] Finally, also the dynamical effects observed in Fig. 3 support this structural assignment: A single row of adatoms is much easier conceived to be displaced laterally than a string of subsurface oxygen atoms in the buckled-row structure.

The process for the formation of the new chemisorption phase can now be summarized as follows: At room temperature oxygen atoms originating from dissociative chemisorption of O_2 diffuse on the terraces of the Cu(110) surface, as do also Cu adatoms which are created by evaporation from terrace regions, mostly at step edges. Because of strongly attractive Cu-O interactions along the [001] direction, nuclei of the (2×1)O phase are formed which consist of a single string of Cu atoms, along [001] on top of the substrate, and which are "glued" together by O atoms in long-bridge positions in between as sketched in Fig. 4(a). This type of nucleus is only of limited stability: It requires a minimum length of about 6 atomic spacings (~25 Å) at room temperature in order to become accessible to STM imaging,[4] and it may fairly easily break up into segments as shown in Fig. 3. These nuclei can be stabilized by additional weak attractions to adjacent steps along [001] or to Cu-O units in next-nearest-neighbor positions along $[1\bar{1}0]$. The latter are also responsible for the growth of these nuclei, with considerably lower probability, in the $[1\bar{1}0]$ direction. The resulting phase is to be denoted more precisely as an added-row rather than a missing-row structure, although both structures are identical with respect to the O and Cu positions within the (2×1)O phase. They differ, however, if the arrangement of these atoms relative to the surrounding nonreconstructed (1×1) terraces is considered—a hopping of single missing-row strings (two missing rows adjacent to one Cu-O row) as seen in Fig. 3 is hardly conceivable. They also differ with respect to the mechanism of their formation: The missing-row reconstruction suggests the removal of Cu atoms from the substrate terraces during (2×1)O formation and their condensation at step sites, while actually these are added by supply from step edges.

In conclusion, it has been shown that the formation of the reconstructed (2×1)O-Cu(110) phase proceeds via a novel mechanism which is based on precipitation of solid nuclei from a two-dimensional fluid phase formed by the chemisorbed species and by adatoms of the substrate diffusing across the surface.

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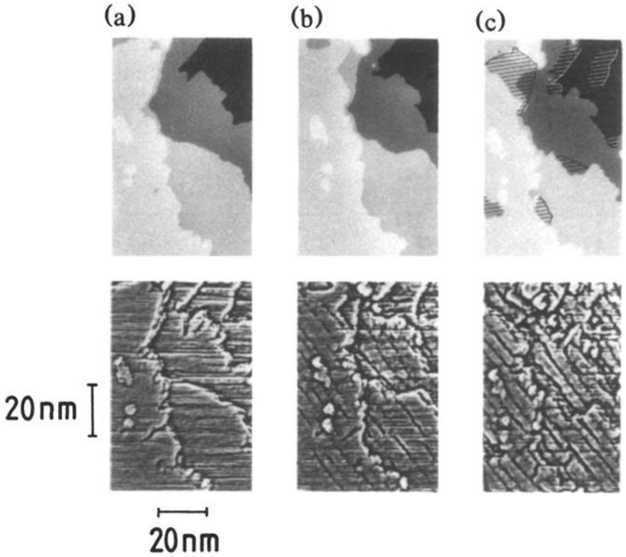

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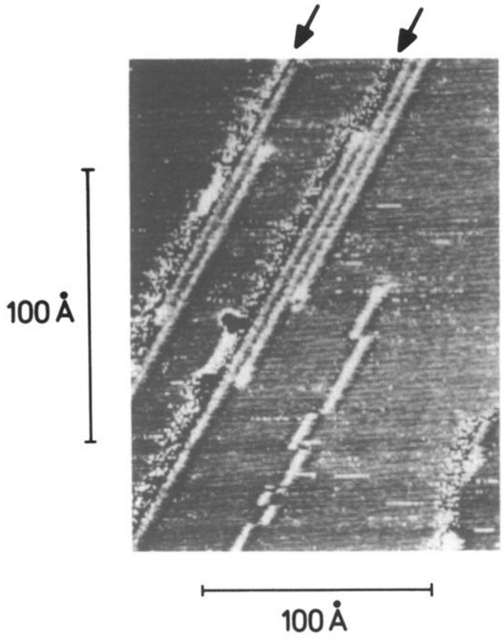

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