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Surface reconstruction of Cu(110) induced by oxygen chemisorption

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The dynamics of the reconstruction of the Cu(110) surface induced by oxygen chemisorption has been studied by scanning tunneling microscopy. The nucleation and growth of the Cu(110)-(2×1)O reconstructed phase shows up as "added rows" of Cu-O atoms which grow preferentially in the [001] direction. The Cu atoms are supplied by diffusion from terrace edges.

Oxygen-induced reconstruction of metal surfaces is a phenomenon which has received considerable attention in the past. This is partly due to its importance for processes like heterogeneous catalysis and corrosion, but it is equally interesting from a more fundamental point of view in the efforts to understand such processes on a microscopic scale.

Oxygen on Cu(110) is one such system which has been studied extensively since the pioneering work of Ertl,[1] who showed that molecular oxygen chemisorbs dissociatively on Cu(110), and that the low-energy electron diffraction (LEED) pattern shows a (2×1) structure at an O coverage of 0.5 ML (monolayers). The half- and integer-order spots of the LEED pattern had comparable intensity indicating a surface reconstruction. However, after more than 20 years of research, the detailed atomic structure of this Cu(110)-(2×1)O surface is still open for debate. Low-energy ion scattering,[2] impact-collision ion-scattering spectrometry,[3] surface-extended x-ray absorption fine structure,[4] He diffraction,[5] and recent x-ray diffraction[6] studies all favor the missing-row reconstruction, where every second [001] row on the surface is absent. On the other hand, the buckled-row model, where every second [001] row is shifted outward, has been suggested by photoemission,[7] high-energy ion scattering,[8] x-ray diffraction,[9] and scanning-tunneling-microscope[10] (STM) data. A recent theoretical calculation based on the effective medium scheme also favors a missing-row-type structure as the most stable one.[11] However, all seem to agree that the oxygen is located at the long bridge positions along the [001] rows.[2,4,8,11,12]

It was the hope when initiating the present study that new information on the dynamics of the surface reconstruction might be obtained, which subsequently might help in understanding the static surface structure.

The experiments were performed with a fully automated STM (Refs. 13 and 14) implemented in an UHV chamber with a base pressure $<1\times10^{-10}$ mbar. The bias voltage is applied to the W tip with the sample grounded, and normally the tip voltage is negative, implying that we are tunneling into empty states in the sample. The initial calibration of the lateral STM scans was obtained from the atomic resolution obtained on the reconstructed Si(111)-(7×7) surface, and the z calibration from a single-layer step on a Si(111) crystal.

After cutting and mechanical polishing down to 1 μm, the Cu(110) crystal was electrolytically polished in dilute phosphoric acid and mounted in the UHV chamber. The surface was cleaned by repeated Ne sputtering and annealing cycles, until no impurities could be detected by Auger electron spectroscopy, and good quality LEED spots indicating a well-ordered (1×1) surface were observed. In most cases the crystal was kept at 100 °C during oxygen exposure, and a constant flow of oxygen through the chamber was maintained to keep a high purity of oxygen.

Figure 1 shows a series of STM images of the surface for increasing oxygen exposure. Here atomic resolution in an STM image of the clean Cu(110) surface was achieved [Fig. 1(a)]. Although the corrugation along the [001] and the [1$\bar{1}$0] rows of this bare surface seems quite small (≤ 0.14 Å), the corrugation is still larger than that measured with the He diffraction technique (0.09 Å).[5] One should keep in mind here, however, as will be discussed further below, that the apparent height of the STM images is a convolution of surface topography and the electronic structure represented as the density of states near the Fermi level. The image of Fig. 1(a) serves to determine the orientation of the sample.

The formation of isolated chains of atoms (interpreted as O-Cu chains) along the [001] direction is initiated when the surface is exposed to oxygen at ≈ 100 °C at exposures ranging from 0.1 to 1 L, where L denotes langmuir (1 L = 10^{-6} Torr sec). It appears that we do not observe any O-Cu chains shorter than $\approx 6\times3.6$ Å, indicating a certain critical minimum length. At higher exposures ($\approx$ 1–2 L) resulting in an O coverage of 0.1–0.2 ML these chains are found in islands developing a unit mesh, with a periodicity which is doubled in the [1$\bar{1}$0] direction [Fig. 1(b)]. Typical dimensions for these islands are 100–200 Å in the [001] direction and 15–20 Å in the [1$\bar{1}$0] direction corresponding to a preferential growth in the [001] direction. This is consistent with the observation of a streaky (2×1) LEED pattern for low oxygen exposure indicating a lack of order in the [1$\bar{1}$0] surface direction. It is evident from Fig. 1(b) and from a large number of similar images, that many of the chains are terminated with what appears as a deep hole or, in a few cases, with a protrusion. These "holes" are tentatively associated with oxygen atoms terminating the Cu-O chains. This is further corroborated by the fact that for images recorded *during* adsorption of oxygen at RT, isolated holes were observed to diffuse on the surface. Further studies are in progress to study this in more detail.

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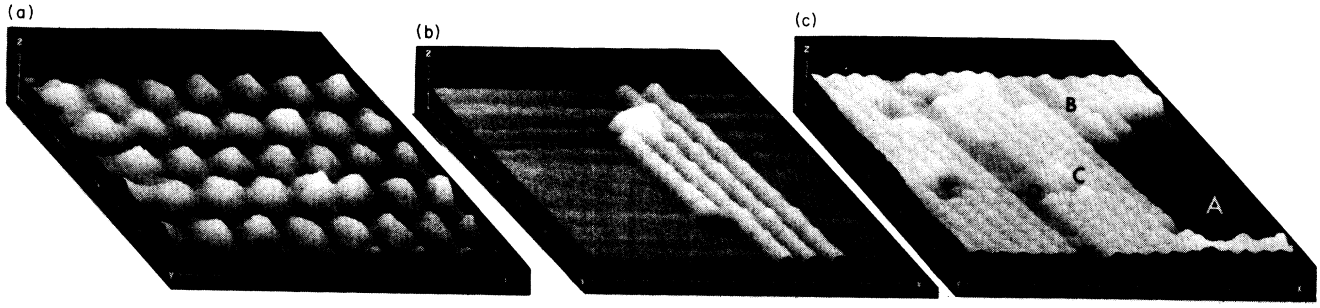

FIG. 1. (a) Atomically resolved STM image of a (20×20)-Å^2 region of a bare (1×1) Cu(110) surface recorded with $V_t = -0.53$ V and $I_t = 2.5$ nA. The z scale is 0.16 Å/division. (b) STM image (70×70 Å^2) showing the formation of added rows after an exposure of ≈ 1 L. The z scale is 0.8 Å/division. (c) STM grey-scale image of a surface area of 100×100 Å^2 after conversion to the (2×1)O reconstructed phase at O exposures of ≈ 10 L recorded with $V_t \approx 0.8$ V and $I_t \approx 0.8$ nA. The z scale is again 0.8 Å/division. In all the pictures the [001] axis coincides with the y axis. The only post-acquisition data processing of the 128×128 pixel images has been a simple two-dimensional nine-point convolution of the raw data.

For exposures to ≈ 10 L causing an O coverage of ≈ 0.5 ML most of the surface is covered with the reconstructed phase, but several types of defects or irregularities may be observed. Figure 1(c) shows some examples. A (reconstructed) terrace (*A*), which is one atomic layer lower, is seen. As expected from the fcc structure of Cu the imaged atoms are shifted by half a lattice unit along the [001] direction and one-quarter of the (2×1) lattice parameter along the [1$\bar{1}$0] direction, relative to the top layer. A single chain of atoms (*B*) between two reconstructed antiphase domains is shifted away from the nearest-neighbor chain by an extra [1$\bar{1}$0] (2×1) lattice parameter. A point defect (*C*) developed from a vacancy is also visible. A region (*D*) between in-phase reconstructed areas, which (with the bias conditions indicated) appears ≈ 0.4 Å lower, shows a very weak corrugation with a periodicity consistent with a $c(6\times2)$ reconstruction.[8] The area of this region is, however, insufficient for any unambiguous determination of the surface unit cell. For extended O exposures up to $\approx 10^5$ L, well-defined $c(6\times2)$ LEED patterns and STM images developed, and further studies are in progress to determine the detailed geometrical structure of this phase.

In the following, we address the question about the growth mode of the reconstructed phase. Figure 2(a) shows two terraces separated by a monatomic step. At this point the Cu(110) surface had been predosed with 1 L of O_2 at 100 °C, and reconstructed islands of Cu-O chains were formed. Then while tunneling at RT we let in oxygen to a pressure of 1×10^{-8} mbar and in Figs. 2(b) and 2(c), recorded after an additional oxygen exposure of 3.15 and 6.3 L, respectively, the edge of the upper terrace has become ragged and removal of Cu atoms from the step is directly visible. It is seen that Cu atoms are removed exclusively from the step edge of the upper terrace between the already formed reconstructed (2×1) islands, and that the rate of removal may be different at different points of the terrace edge. We observe a simultaneous growth of the reconstructed islands on the lower terrace, preferentially along the [001] direction. This leads us to the conclusion that the reconstructed phase grows on top of terraces by nucleation of Cu atoms diffusing from step

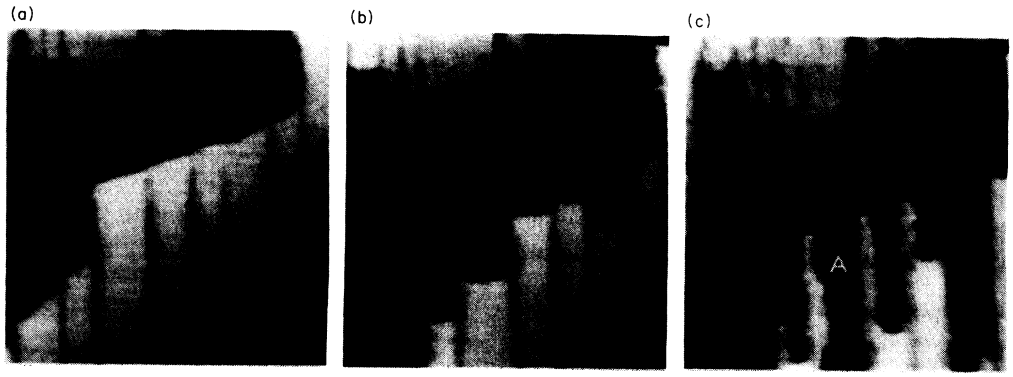

FIG. 2. Series of STM grey-scale images over an area of 1000×1000 Å^2 showing dynamical growth of the reconstructed phase. (a) The Cu(110) surface has been exposed to 1 L of O_2 at 100 °C and small islands of the reconstructed Cu(110)-(2×1)O phase are directly visible (dark stripes). (b) and (c) were recorded after the surface had received an additional oxygen exposure at 10^{-8} mbar at RT (while tunneling) for 420 (3.15 L) and 840 sec (6.3 L), respectively. A small drift is observed in the STM images between (a) and (c). The images were recorded with $I_t \approx 0.7$ nA and $V_t \approx 0.5$ V, which explains why the reconstructed (2×1) islands show up as troughs rather than added rows (cf. text).

edges and O atoms diffusing on the surface.

The removal rate of Cu atoms from step edges during oxygen exposure can be estimated from a series of STM images of the terrace-edge region. It turns out that in many cases the removal rate exceeds, by at least an order of magnitude, the impingement rate of O_2 molecules in an area around the terrace edge. Unless the impinging O_2 molecules have an extreme efficiency for Cu removal, this must indicate that diffusion of oxygen on the surface also plays a major role in the formation of the reconstruction.

Although the "added-row" and the "missing-row" models are identical at the saturation coverage (0.5 ML), they deviate significantly in terms of mass transport and for lower coverages. For the added-row model, the Cu atoms are supplied from step edges as seen in Fig. 2, while the missing row would lead to a mass transport from terraces to, e.g., step edges. That Fig. 2 actually reflects the diffusion of Cu atoms from the topmost terrace, and not an electronic structure artifact caused by O, is confirmed by the observation that area (A) from which Cu atoms have been removed on the topmost terrace exhibits a well-resolved (1×1) STM image.

The [001] oriented chains or added rows of Cu and O atoms are formed by fairly strong attractive interaction between the O and Cu atoms. This interaction appears to be strongest along the [001] direction, with the O atoms located in long bridge positions between Cu atoms. The stability of Cu-O rows increases if several chains group together and a two-dimensional unit mesh develops as, e.g., seen in Fig. 1(b). The assignment of the reconstruction as an added-row type is supported by recent theoretical calculations[11] which find that the oxygen $2p$ states hybridize more strongly with d states on metals with a low coordination number. Thus, for oxygen chemisorption during formation of the reconstructed phase, the long bridge site in an added row is energetically more favorable than in the first layer of Cu atoms.

Displacements of chains at room temperature are often observed between consecutive images of the same area. Both displacements of single chains, either isolated or at the edge of reconstructed islands, and collective displacements of a group of chains are seen. The great mobility of the chains supports the hypothesis that they are actually situated on top of the (1×1) surface as predicted by the added-row model. In certain cases the STM images display the chains as segments displaced from each other along the $[1\bar{1}0]$ direction. Contrary to the interpretation in Ref. 15, this should not necessarily be taken as evidence for fragmentation of the chain. It may simply indicate that the hopping time for the chain structure is much smaller than the time needed for imaging the surface. This interpretation is corroborated by Fig. 3, which shows three consecutive images of a chain segment at the end of a nucleus three chains wide. The images show the segment moving from one chain to the next. A detailed analysis of Fig. 3(b) showed that the segment was imaged at *both* positions for one particular line scan. This indicates that the segment has hopped the ≈ 5 Å-distance in less than ≈ 1 msec, corresponding to an equivalent diffusion constant $D \geq 10^{-13}$ cm^2/sec.

In the STM study by Chua, Kuk, and Silverman,[10] it is argued that the Cu(110)-(2×1)O reconstruction is associated with a buckled-row model in which alternate [001] Cu rows are displaced outward by 0.8 ± 0.2 Å from the first layer. This model is, however, clearly inconsistent with the diffusion of Cu atoms from step edges and the large mobility of the Cu-O chains. Further support for the added-row model was found in the present study by the application of Fourier transform and averaging techniques to images recorded in the interface region between the (1×1) and the (2×1) phases, where the atomic resolution was insufficient for a simple, visual analysis. The troughs between the Cu-O chains were found between the (1×1) unit mesh lattice positions. If the reconstruction had been of the missing-row type, the troughs would coincide with lattice positions.

Contrary to the results by Chua *et al.*,[10] reporting an insensitivity of the measured vertical heights to changes in tip voltage, we find it impossible to derive reliable height information (topography) from the STM images. From a large number of images recorded with W and Pt/Ir tips it was typically so that the reconstructed phase would show up as protrusions, i.e., added rows in one bias-voltage interval, typically ≥ 1 V; whereas, if the same area was scanned in another bias interval (less than ≈ 0.6 V), the chains showed up as troughs, i.e., actually appeared lower than the surrounding, unreconstructed surface.

In the course of this work we became aware of the independent work by Coulman *et al.*[15] on the same system. The conclusions reached by them are very similar to those drawn by present work.

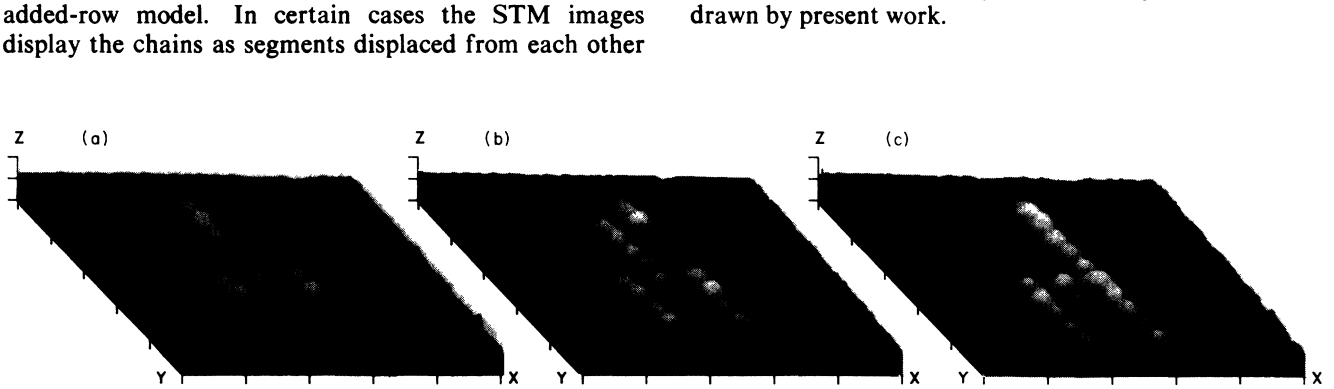

FIG. 3. STM images over an area of 50×50 Å^2, recorded with $V_t \approx 0.4$ V and $I_t \approx 1.0$ nA. The three images, formed by line scans in x, are taken at 3-sec intervals. The dynamical movement of a single Cu-O chain segment between the three chains is directly visible.

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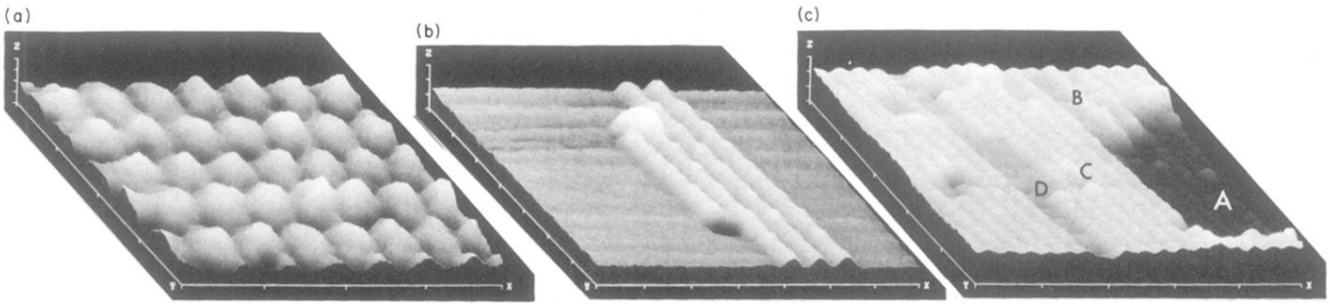

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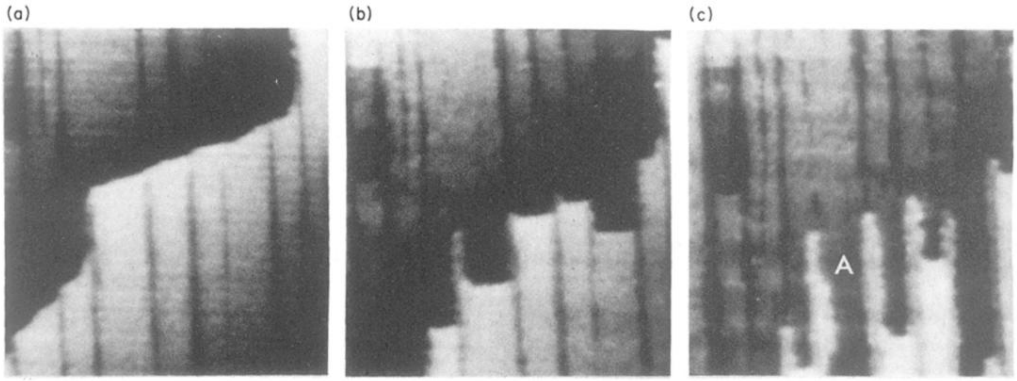

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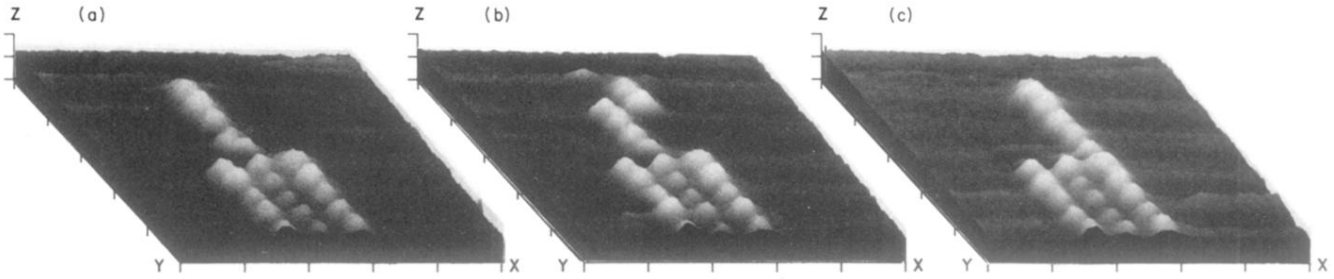

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