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N-induced (2 × 3) reconstruction of Cu(110): Evidence for long-range, highly directional interaction between Cu—N—Cu bonds

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The scanning-tunneling-microscope (STM) topographies taken from a N-induced (2×3) reconstructed Cu(110) surface provide unique information, which offers the basis for an explanation of the peculiar fact that every third $\langle 110 \rangle$ row is missing and also confirm in detail the structural model inferred from recent ion-scattering measurements. The close analysis of STM images with atomic resolution taken from both ordered (2×3) domains and local defective arrangements evidences the existence of long-range, highly directional interactions between Cu—N—Cu bonds, which seems to determine ultimately the nature of the reconstruction.

Heskett *et al.* have recently reported on a low-energy electron-diffraction (LEED), thermal-desorption spectroscopy (TDS), and high-resolution electron-energy-loss spectroscopy (HREELS) study of the adsorption of atomic nitrogen on Cu(110).[1] Upon annealing the N-loaded surface to 600–700 K, they found that "the nitrogen overlayer exhibits a very sharp and stable (2×3) LEED pattern and unusual thermal desorption behaviour." These results were interpreted "as indicating a nitrogen-induced reconstruction of the Cu(110) surface." In addition, based on the HREELS data, the nitrogen atoms were assigned to be bonded in the long bridge position sites and, similar to the bulk copper nitride, Cu_3N complexes may be formed. In spite of this important information, the applied methods did not allow the proposal of a reconstruction model.

Very recently we investigated the same system by using as a principal tool the 180° low-energy-impact-collision ion-scattering spectroscopy with detection of noble gas neutrals (180° NICISS).[2] The main attribute of this method is to supply mass selectively the relative locations of atoms in the first few surface layers, while keeping the radiation damage at a negligible level.[3] The NICISS patterns demonstrate unequivocally that the nitrogen induces a reconstruction of the Cu surface, confirming the interpretation in Ref. 1. In addition, from the determined relative locations of the Cu atoms, the reconstruction model shown schematically in Fig. 1 has been constructed. It is a missing-row model with every *third* $\langle 110 \rangle$ row missing. This leads to the threefold periodicity in the $\langle 001 \rangle$ direction as observed by LEED. The twofold periodicity in the $\langle 110 \rangle$ direction cannot, however, be traced back to the locations of the Cu atoms as deduced by the NICISS patterns. Thus the twofold periodicity in the $\langle 110 \rangle$ direction has to be ascribed to the arrangement of the N atoms. The particular arrangement chosen in Fig. 1 has been suggested by their location in the long bridge sites referred from HREELS,[1] from a peak shift in the NICISS patterns in the $\langle 001 \rangle$ azimuth,[2] and the N coverage of less than one quarter of a monolayer ($\frac{1}{4}$ ML) as obtained from Auger electron spectroscopy (AES) measurements.[2] The exact locations of light adsorbates, however, by NICISS is hardly possible, so that the N-atom arrangement chosen in Fig. 1 remained somewhat speculative.

The scanning tunneling microscopy (STM) investigation presented here confirms impressively the structure model in Fig. 1. In particular, it excludes the fourfold hollow site as a location for the N atoms. The unique capabilities of the STM allow the detailed exploration of local structural defects, which are hardly accessible to other methods. The particular structure of these defects gives us strong evidence for a very characteristic long-range interaction between Cu—N—Cu bonds, which is probably the origin of the rather peculiar structure shown in Fig. 1: every *third* $\langle 110 \rangle$ Cu row is missing and the N atoms, while located in each second bridge position along $\langle 110 \rangle$, are *aligned* in the $\langle 001 \rangle$ direction in spite of a large mutual distance of 10.8 Å.

The measurements were performed in a small ultrahigh

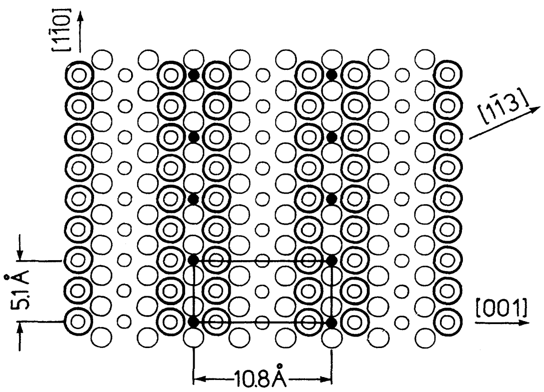

FIG. 1. Surface structure model of the nitrogen-induced (2×3) reconstructed Cu(110) surface. On top, view of the first four monolayers: bold circles, first-layer Cu atoms; solid dots, nitrogen atoms in the long bridge position. The unit cell of the (2×3) structure is indicated.

vacuum (UHV) chamber with a commercial "beetle-type" STM.[4] The sample could be moved *in situ* from the STM into a position where it could be sputtered and annealed. All measurements were performed at room temperature. The piezoceramic elements have been calibrated by a procedure described in detail elsewhere;[5] the lateral X,Y magnification factors have been determined by imaging the well-known Si(111)-(7×7) surface. Although performed in a different UHV chamber, the STM measurements were made on the same Cu crystal and with the same sample preparation procedure as in the previous NICISS investigation.[2] Prior to each experimental run, the sample was cleaned by sputtering and subsequent annealing at 700 K, resulting in a sharp (1×1) LEED pattern and a clean surface as determined by AES. This surface imaged with atomic resolution is shown in Fig. 2. The gray scale image for a 32×32 Å^2 area has been obtained in the constant current mode ($i=5$ nA) with a tip-to-sample voltage of -40 mV. The measured maximal corrugation (normal to the surface) is 0.3 Å and even the Cu atoms in the close-packed $\langle 110\rangle$ rows are well resolved.

As already described in detail,[1,2] the nitrogen-induced (2×3) phase cannot be produced by molecular N_2 adsorption but was obtained by bombarding the crystal with 200-eV N^+ at 300 K for about 60 sec and, after annealing at 650 K, a sharp (2×3) LEED pattern is observed which remained extremely stable over several days. Implantation of nitrogen at higher energies (e.g., 500-eV N^+) and subsequent annealing never produced a smooth large area (2×3) surface. At best, the entire surface was covered with small islands separated by steps. The islands were on average 100–200 Å long in the $\langle 110\rangle$ directions and about 40–100 Å wide. The resulting surfaces, although being covered completely with the N-(2×3) phase [good LEED (2×3) pattern], were very rough and thus not well suited for a closer investigation of the structure. Accordingly, in all the STM images presented below the nitrogen has been implanted at 200 eV.

In Fig. 3 we show an area of 1100×1100 Å^2 with a linear structure (parallel to the $\langle 110\rangle$ direction) running from the upper left side to the lower right side. As will become apparent from the higher-resolution images presented below, the lines are structured to chains consisting of two $\langle 110\rangle$ rows of close-packed Cu atoms with the N atoms in between. This chain structure is distributed in islands separated by interatomic steps 1.3 Å high. The step boundaries of the islands are often irregular. However, in several STM images we have taken, as, e.g., in Fig. 3, the island step boundaries appear to prefer to follow straight lines (in some cases over more than 1000 Å) which are aligned along high-symmetry directions of the (110) surface. One of the linear island boundaries is always oriented along the $\langle 110\rangle$ directions, i.e., parallel to the chains, as could be expected. Surprising at first glance is that the other island boundaries are oriented approximately along $\langle 113\rangle$ directions, and in some cases we also find them along $\langle 001\rangle$ directions. A closer look at the model in Fig. 1 solves the puzzle: all these directions allow the chains to terminate with the same configuration, either with a Cu-Cu or Cu-N-Cu complex.

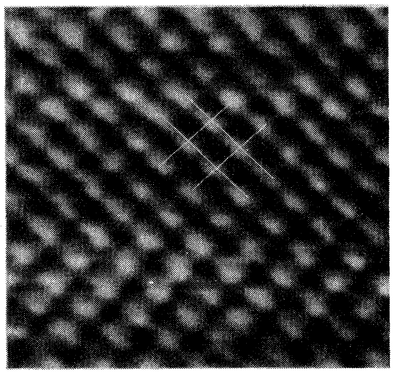

FIG. 2. High-resolution STM image of the clean Cu(110)-(1×1) surface. The area of 32×32 Å^2 is shown as measured in the constant current mode. The unit cell of 3.61×2.55 Å^2 is schematically indicated. $U_{\text{tip}}=-40$ mV, $i=5$ nA.

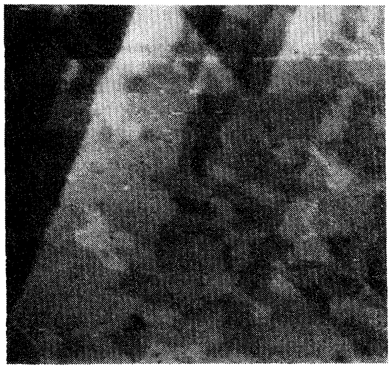

FIG. 3. STM survey image of a 1100×1100 Å^2 area of the Cu(110)-(2×3) surface. $U_{\text{tip}}=+900$ mV, $i=1$ nA.

Higher-resolution images like that shown in Fig. 4 (370×370 Å^2) demonstrate in fact the mentioned chainlike structure. The distance between equidistant chains is determined from the STM image to 11 Å in the $\langle 001\rangle$ direction. The distance between two minima within each chainlike structure in the $\langle 110\rangle$ direction is measured to 5 Å. This is very close to the dimensions of the (2×3) unit cell of 10.8×5.1 Å^2 as deduced from the schematic structure shown in Fig. 1. Consequently, the graphic representation of the two-dimensional Fourier transform of a topograph like that in Fig. 4 appears to be very similar to the (2×3) measured LEED pattern.

In order to explore the details of the structure, we have zoomed further and obtained images like that shown in Fig. 5 (52×52 Å^2). Each chain link consists of a center oval black hole enclosed between four bright spots. The distance between the spots is approximately 3.5 and 5 Å in the $\langle 001\rangle$ and $\langle 110\rangle$ directions, respectively. In view of the structure model in Fig. 1, where the relative positions of the Cu atoms are accurately determined from the NICISS patterns, the bright spots in the STM image can be faithfully associated with Cu atoms. Note, however, that unlike the nonreconstructed Cu surface shown in Fig. 2, not all Cu atoms present in the close-packed $\langle 110\rangle$ rows (mutual Cu-Cu distance 2.55 Å) are imaged

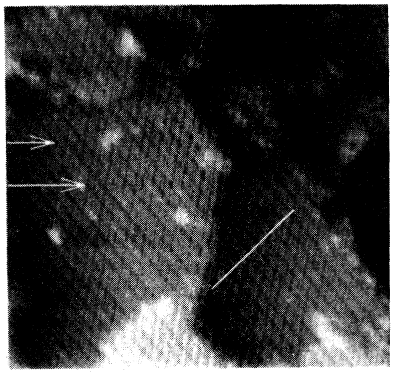

FIG. 4. STM image of the N/Cu(110)-(2×3) surface. Surface area 370×370 Å^2. White line, phase boundary between two (2×3) domains displaced by 3.6 Å in the ⟨001⟩ direction. Arrows mark a defective segment with adjacent chain structure (see text). $U_{\text{tip}} = -120$ mV, $i = 1$ nA.

in Fig. 5; instead every other Cu atom is imaged. Knowing positively from the NICISS measurements that the mutual positions of the Cu atoms within the ⟨110⟩ rows on the (2×3) reconstructed surface are practically the same as on the nonreconstructed (1×1) surface, the absence in the STM image of every other Cu atom in the ⟨110⟩ rows cannot result from a topographic effect, but has to be ascribed to the influence of the N atoms. It appears that the change in the electronic state of a Cu atom due to the bonding to the N atom changes its "visibility" in the STM pattern.[6] STM images are often very suggestive so that we are inclined to associate the holes in the chains with the location of the N atoms. Because we cannot verifiably decide so far whether the Cu—N bond diminishes or enhances the visibility of the Cu atoms involved, the position of N may as well be between the bright spots. In any case, from the fact that the visibility of every other Cu atom is changed, we can clearly discard the fourfold site for nitrogen and conclude that the N atoms are located in the long bridge position in agreement with Ref. 1 (cf. Fig. 1).

Another important observation in Figs. 4 and 5 has to be emphasized here: *all* chains, though separated by 10.8 Å, are perfectly in phase (i.e., not mutually shifted along the ⟨110⟩ direction) and consequently the holes (or the protrusions, respectively) are aligned in the ⟨001⟩ directions over distances of hundreds of angstroms. This observation not only supports the arrangement of the N atoms in the structure model in Fig. 1, which was primarily aimed at providing the double periodicity in the ⟨110⟩ direction, but it is particularly interesting *per se*. Namely, it implies a strong interaction between Cu—N—Cu bonds separated by a distance of more than 10 Å. This situation clearly favors the colinear location of the Cu—N—Cu bonds with respect to a location mutually shifted by one lattice spacing in the ⟨110⟩ direction.

The unique capabilities of the STM can be used also to explore details of defects present on any real surface. One example can be recognized on the otherwise largely defect-free (2×3) terrace in the lower right quadrant in Fig. 4. It is a phase boundary (white line) separating two (2×3) domains shifted mutually by 3.6 Å in the ⟨001⟩ direction, i.e., by a phase difference of $2\pi/3$.

Another type of defect, which uncovers additional basic features of the interaction between the Cu—N—Cu bonds, can be noticed at a few places on the large terrace filling the left side of Fig. 4: on segments with lengths of the order of 100 Å, pairs of chains are close together, instead of being separated by a "missing row" (their mutual distance is 7.2 Å instead of 10.8 Å). A zoomed image of such a defected region is shown in Fig. 6 (52×52 Å^2). The striking observation is that, in contrast to the normally separated (10.8 Å) chains, *all* adjacent (not separated) chains are mutually shifted, i.e., they are staggered, in the ⟨110⟩ direction by one lattice spacing of 2.55 Å: for all adjacent chain pairs (defected) we have observed this phase shift by following, as exemplified in Fig. 6, a ⟨001⟩ oriented line. The obvious conclusion is that the mutual interaction between Cu—N—Cu bonds, which favors their colinear location at 10.8 Å, excludes the colinearity for a distance of 7.2 Å in favor of a shifted location. From the fact that segments of adjacent chains are rather the exception and at most double chains occur (defects), we infer further that the colinear location of the Cu—N—Cu bonds at 10.8 Å is energetically favored with

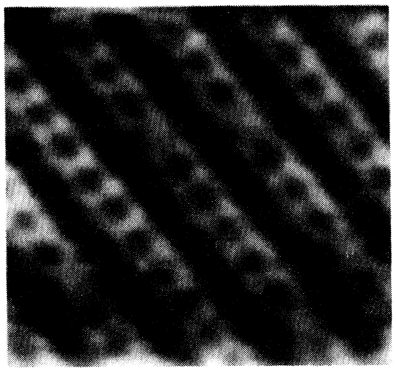

FIG. 5. High-resolution STM image of the N/Cu(110)-(2×3) surface. Surface area 52×52 Å^2. $U_{\text{tip}} = -120$ mV, $i = 1$ nA.

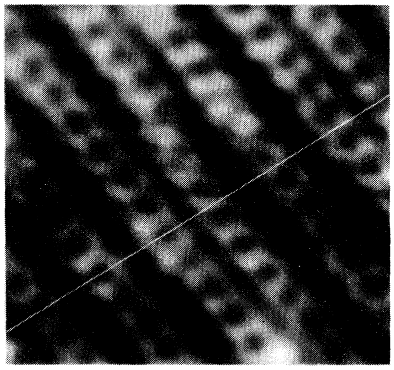

FIG. 6. High-resolution STM image of the N/Cu (110)-(2×3) surface showing imperfections in the (2×3) periodicity. Surface area 52×52 Å^2. $U_{\text{tip}} = -120$ mV, $i = 1$ nA.

respect to the shifted location, where the bonds are in fact 7.6 Å apart. The small difference between the interbond distances of the forbidden colinear arrangement (7.2 Å) and the allowed shifted one (7.6 Å) in the case of adjacent chains, as well as the clearly favored colinear arrangement in the case of separated chains, indicates not only the long range but also the highly directional character of interaction between the Cu—N—Cu bonds. These distinctive properties of the interaction of Cu—N—Cu bonds seem to determine ultimately the peculiar atomic structure of the nitrogen-induced (2×3) reconstruction.

In summary, the STM investigation not only fully confirms the (2×3) missing-row model based on ion-scattering measurements, but also supplies information needed to explain the "peculiar" fact of every third $\langle 110\rangle$ Cu row missing. In particular, it excludes the fourfold hollow site position for the N atoms and confirms the bridge location as also deduced from HREELS measurements. The double periodicity in $\langle 110\rangle$ directions is directly visible in the STM images and in accordance with the arrangement of the N atoms along $\langle 001\rangle$ lines separated by 5.1 Å. From the detailed analysis of the mutual distribution of the chainlike $\langle 110\rangle$ rows on ordered terraces and on defected regions, a strong, highly directional correlation between Cu—N—Cu bonds extending over more that 10 Å has been found. The rich features of this interaction seem to determine the nature of the N-induced (2×3) reconstruction of the Cu(110) surface. Finally, this study demonstrates the synergistic effectiveness resulting from the combined use of two real-space methods (NICISS and STM) with complementing capabilities.

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[1] D. Heskett, A. Baddorf, and E. W. Plummer, Surf. Sci. **195**, 94 (1988).

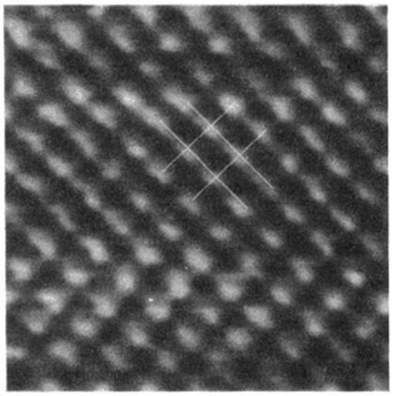
[2] R. Spitzl, H. Niehus, and G. Comsa (unpublished).

[3] R. Spitzl, H. Niehus, and G. Comsa, Rev. Sci. Instrum. **61**, 2 (1990).

[4] K. H. Besocke, Delta Phi Electronic, Postfach 2243, D-5170 Jülich, Germany.

[5] H. Niehus, W. Raunau, K. Besocke, R. Spitzl, and G. Comsa, Surf. Sci. **225**, L8 (1990).

[6] The imaging of this electronic structure, which reflects the electronic properties of the Cu—N bond, appears to be spectroscopically sensitive. The structure is only visible at low (−200 to 200 mV) tip bias; at higher voltages the chainlike rows appear structureless.



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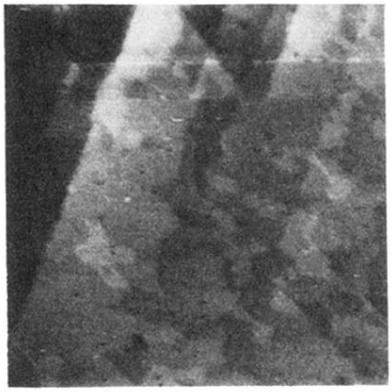

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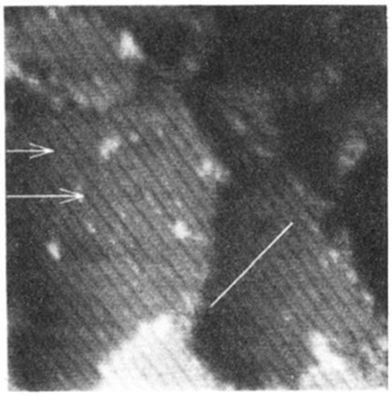

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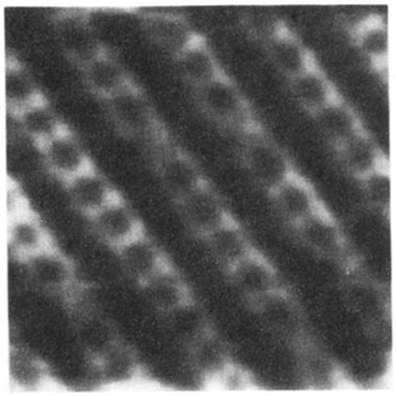

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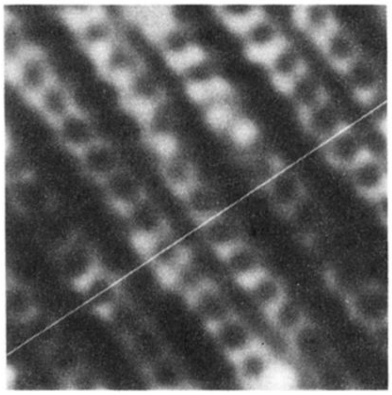

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