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Determination of the reconstruction of Cu(110)-(2×3)-N with high-energy ion scattering

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Surface yield measurements with single-alignment high-energy ion scattering, at normal incidence, are used to show that the Cu(110)-(2×3)-N surface is reconstructed according to an additional-row model, where the first-layer density of Cu atoms is increased to $\frac{4}{3}$ monolayers. A surface-reconstruction model involving missing rows can be excluded. We also find that $\frac{2}{3}$ of the second- and third-layer atoms are displaced laterally, from their bulklike positions, by 0.30 and 0.07 Å, respectively. Off-normal-incidence measurements indicate additional vertical atomic displacements in the second and third layers.

One of the central issues in surface science is the determination of geometric surface structure, which is a cornerstone in any further understanding of the processes occurring at surfaces. Since we cannot directly image atomic cores at surfaces, structural models obtained from investigations employing different techniques sometimes contradict each other. One such case is the nitrogen-induced (2×3) reconstruction of the Cu(110) surface, which has attracted much attention recently. As a consequence of the efforts of several investigators, three uniquely different models have been proposed. Using photoelectron diffraction and low-energy ion scattering (LEIS), Robinson *et al.*[1] and Ashwin and Woodruff[2] suggested that the surface is reconstructed by forming a squarelike (100) overlayer. This model introduces an additional [1$\bar{1}$0] row into the first layer and increases the atomic density to $\frac{4}{3}$ monolayers (ML). Based on scanning tunneling microscopy (STM) and LEIS results, Niehus *et al.*[3] and Spitzl, Niehus, and Comsa[4] instead proposed a missing-row reconstruction, where every third [1$\bar{1}$0] row of Cu atoms is missing in the [001] direction, thus reducing the atomic density in the first layer to $\frac{2}{3}$ ML. A third model derived from a low-energy electron diffraction (LEED) study by Grimsby, Zhou, and Mitchel[5] involves missing [001] Cu rows. An x-ray-diffraction study by Baddorf *et al.*[6] confirmed the additional-row model but also showed that the first layer exhibits a large vertical buckling. This model also involves significant vertical displacements of subsurface layers. It was proposed that the first-layer buckling can explain the features observed with STM. Recent STM measurements by Leibsle, Davis, and Robinson[7] suggest that the reconstruction may actually be different at low and high N coverage. Because of this lack of consensus, a new and different structural investigation of the substrate reconstruction is necessary. In this paper, we focus on the substrate reconstruction at *N* saturation coverages. The results may have important implications for other systems,[8,9] like Ni(100), where a (2×3) reconstruction has been interpreted in terms of a missing-row model.[9]

The characteristic difference between the proposed models is the density of first-layer Cu atoms. While in the missing-row models the first layer is in registry with the substrate, the increased density in the additional-row model results in lateral displacements of these first-layer atoms from bulklike positions, larger than 0.3 Å.[1,2,6] It is exactly this fact which enables us to differentiate between the models, using single-alignment high-energy ion scattering (HEIS).[10] In the MeV energy range, scattering cross sections are accurately known and an absolute measurement of the number of atoms visible to the incident ion beam is possible. Surface sensitivity is achieved by aligning the ion beam along a main crystallographic axis. This results in shadowing of atoms in deeper layers and only the topmost atoms contribute to the backscattering yield. Atoms displaced in the top layer perpendicular to the incidence direction reduce this shadowing and the scattering yield increases.[10,11] If the ion beam is aligned along the normal incidence [110] direction, we expect an increased scattering yield compared to the unreconstructed clean surface for the additional-row model, and relatively little, if any, increase for the missing-row models.

Measurements have been made for several ion-beam energies. The measured increases for all ion energies clearly rule out any missing-row reconstruction. However, the observed backscattering yields are even higher than expected for the additional-row model, where $\frac{4}{3}$ ML of Cu atoms in the first layer are out of registry with the underlying substrate. This shows that subsurface Cu atoms are displaced laterally from their bulklike positions. The magnitudes of the shifts were determined by comparing the measured backscattering yields to Monte Carlo calculations. We obtain lateral shifts of 0.30 and 0.07 Å for second- and third-layer atoms, respectively. Similar measurements with the ion-beam aligned along the off-normal [101] direction indicate additional large vertical shifts of subsurface atoms.

The experiments were carried out in an ultrahigh vacuum chamber with a base pressure of 1×10^{-10} Torr. It was equipped with instrumentation for LEED and

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Auger-electron spectroscopy, an ion sputter gun, a mass spectrometer, and was linked to a 2.5 MeV Van de Graff accelerator. Two circular apertures (1 mm diameter) collimated the He ion beam to a divergence of ca. 0.02°. Scattered ions were detected by a surface-barrier detector with a 1×5 mm^2 aperture. The sample was mounted on a two-axis goniometer and could be heated by electron bombardment. It was cleaned by cycles of 500-eV Ne ion sputtering and subsequent annealing to 450 °C. Following earlier studies,[12] the saturation (2×3)-N structure was prepared by sputtering the sample with 200-eV-nitrogen ions and subsequent annealing to 400 °C, a temperature sufficient to anneal defects created during Ne ion sputtering, to desorb excess nitrogen. After that, the surface displayed a well-ordered (2×3) LEED pattern. We used N ion doses ranging from 2700–22000 μC. Since the sample was mounted in electrical contact with a larger base plate, we estimate the actual ion dose on the sample surface to be lower. All doses gave identical HEIS results, indicating that the substrate reconstruction does not change in this deposition range. The HEIS measurements were performed with the sample at room temperature. To convert the measured scattering yield into Cu atoms/row, we used standards with a known areal density of Cu or Sb implanted into silicon substrates.

In Fig. 1, typical HEIS spectra for the clean (open circles) and reconstructed (solid circles) surface are shown. The spectra were obtained for 0.6-MeV-He ions impinging onto the sample along the normal incidence [110] direction. Due to the very different cross sections for Cu and N, the spectra are dominated by the scattering of He ions from Cu atoms. Projectiles, elastically scattered from Cu atoms at the surface contribute to the peak (surface yield) at 0.5 MeV. Its width is determined by the detector resolution of ca. 25 keV and the different Cu isotopes in the crystal. A small peak at 0.43 MeV is due to beam steering effects for channeled ions in the crystal.[11,13] The observed increase in the surface yield of 45% for the reconstructed surface relative to that of clean Cu(110), shows that more surface atoms are exposed to the incoming ions. To first order, a missing-row reconstruction does not change the surface yield since the in-plane registry of the surface atoms is not changed. However, due to different vibrational amplitudes and small lateral displacements of subsurface atoms, the yield can increase slightly. To obtain an estimate of the surface yield that can be expected for a missing-row model, we measured the yield from the (2×1)-O structure as a reference, where the reconstruction is known to involve missing rows.[14] The surface yield of the (2×1)-O structure is 6% higher than that of clean Cu(110), corroborating earlier results.[15] The large surface yield for Cu(110)-(2×3)-N, therefore, clearly favors the additional-row model.

For a quantitative analysis, we converted the measured surface yields into visible atoms/row, after subtracting the background of dechanneled ions.[13] The results are displayed in Fig. 2 for the clean (open diamonds) and reconstructed (solid diamonds) surfaces for various incident ion energies. We performed Monte Carlo simulations of the scattering from a row of atoms,[11,16] for an accurate comparison with the surface yields expected for the different reconstruction models. The clean Cu(110) surface can be viewed as being composed of atomic rows

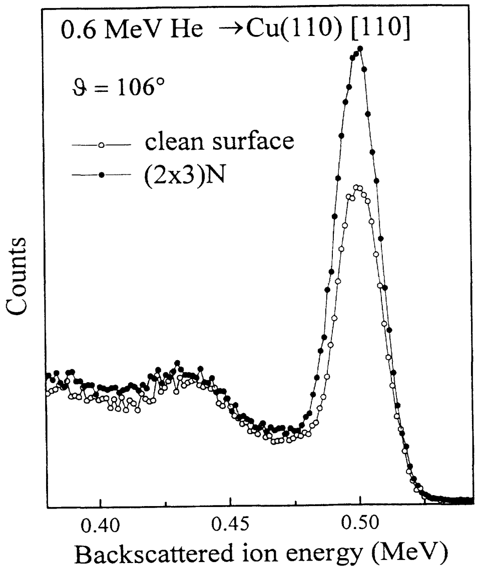

FIG. 1. Spectra obtained for 0.6-MeV-He ions backscattered from Cu(110) with the beam aligned along the [110] normal incidence direction. The detector was positioned at a scattering angle of 106°. Ions, elastically scattered from Cu surface atoms, cause the peak at an energy of 0.5 MeV. The elastic N peak, which is expected to be at 0.41 MeV, is not distinguishable from the background due to the much lower scattering cross section for nitrogen compared to copper.

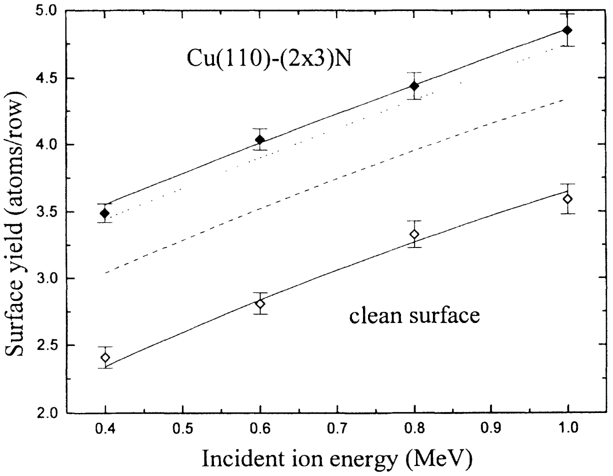

FIG. 2. Surface yield of He ions backscattered from Cu surface atoms versus incident beam energy. The surface yield was obtained by integrating the elastic Cu peaks shown in Fig. 1 and was converted into visible atoms/row as described in the text. The symbols show the measured yield from the clean (open diamonds) and nitrogen reconstructed surfaces (solid diamonds). Also shown is the calculated yield for an unreconstructed surface (lower solid line), an unreconstructed surface covered with a $\frac{4}{3}$ ML of Cu according to the additional-row model (Ref. 6) (dashed line) and the additional-row model with lateral displacements of second-layer atoms (dotted line) and also third-layer atoms (upper solid line).

normal to the surface. There are two [110] rows of atoms per (1×1) unit cell, one terminated in the first layer and the other in the second. In HEIS, the size of the shadow cast by the top-layer atom at the positions of the atoms beneath is of the order of the thermal atomic vibrational amplitude.[11,13,16] For this reason, the second and third atoms in each row contribute significantly to the surface yield, which accounts for values larger than one, even for the clean surface. In the calculations, bulk values of the thermal vibration amplitudes were used. Including enhanced vibrations for surface atoms changed the results insignificantly. A variation of the ion energy changes the size of the shadow and, therefore, the surface yield. This behavior is very well reproduced by the calculations for the unreconstructed clean surface (lower solid line in Fig. 2).

On a surface which is reconstructed according to the additional-row-model, the top layer is out of registry with the substrate. At normal incidence, the top-layer atoms are, therefore, laterally shifted from the [110] atomic rows. In order to simulate this effect, we displaced the first atom in a row and calculated the backscattering yield. The results are shown in Fig. 3, for the ion energies used in our experiment. When the top-layer atom in the row is displaced laterally, the shadowing of subsurface atoms is reduced and the surface yield increases. If the displacement is large enough so that the second-layer atom passes through the edge of the shadow, flux focusing occurs and is responsible for the enhanced yield around 0.3 Å observed in Fig. 3.[17] With increasing energy, this yield enhancement is shifted towards smaller displacements as a consequence of the varying shadow size. The calculations in Fig. 3 also show that for displacements larger than ca. 0.6 Å the backscattering yield can be described as being due to backscattering from an atomic row and one additional isolated atom.

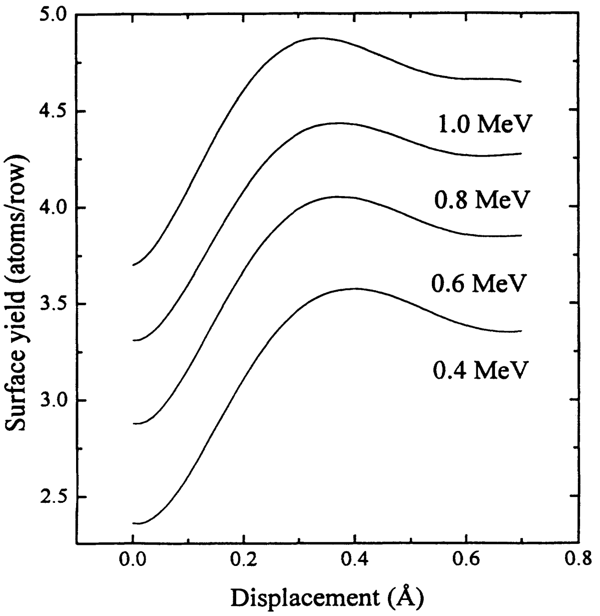

FIG. 3. Surface yield for ions scattered from a row of atoms as a function of the displacement of the top atom perpendicular to the row. Shown are the results for several ion energies.

Using the results shown in Fig. 3, we can now calculate the surface yield for the (2×3)-N reconstruction, assuming the atomic positions given by Baddorf *et al.*[6] A side view along the [001] direction of their model is reproduced in Fig. 4. While the threefold periodicity in [001] direction is caused by the substrate reconstruction, the twofold periodicity in the $[1\bar{1}0]$ direction is caused by the N overlayer[6] (not shown in Fig. 4). The (2×3) unit cell, therefore, contains twice the number of atoms shown in Fig. 4, i.e., there are eight first-layer atoms. The substrate is composed of twelve atomic rows per unit cell. Half of them terminated in the second layer and half in the third. The increase in backscattering yield caused by the first-layer atoms has to be averaged over these twelve rows. Due to the C_{2V} symmetry of the surface, there are two inequivalent atoms in each layer. The first-layer atoms *A* are laterally close enough (0.3 Å) to an atomic row, starting in the third layer, in order to cause a flux focusing (see Fig. 3). They, therefore, contribute 1.1–1.2 atoms/row, depending on the ion energy, to the backscattering yield, whereas atoms *B* contribute 1.0 atom/row. The resulting averaged increase in the surface yield is shown by the dashed line in Fig. 2. This is, however, lower than the measured yields. We, therefore, conclude that lateral displacements in subsurface layers occur. The simplest subsurface atomic movements compatible with the C_{2V} symmetry of the surface are displacements in the [001] direction for the second-layer atoms labeled *C* in Fig. 4 and third-layer atoms beneath atoms *A*. Displacements of second- and third-layer atoms in the $[1\bar{1}0]$ direction would significantly alter the bulklike nearest-neighbor distance in this direction and are, therefore, less likely to occur. The inclusion of [001] displacements of atom *C* by 0.30 Å results, according to Fig. 3, in a total surface yield described by the dotted line in Fig. 2, which is still slightly lower than the experimentally observed values. We obtain excellent agreement with experiment by introducing an additional third-layer displacement of 0.07 Å (upper solid line in Fig. 2). This displacement pattern is not unique, e.g., a slightly smaller second-layer shift can, to some extent, be compensated by a larger third-layer displacement. Since, however, the displacement amplitude usually decays rapidly with the distance from the surface, we dismiss this alternative and favor the model with the smallest third-layer shift. Keep-

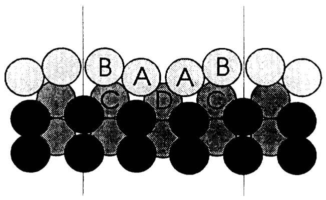

FIG. 4. Side view along the [001] direction of the surface reconstruction according to the additional-row model of Ref. 6. The N overlayer (not shown) causes the twofold periodicity in $[1\bar{1}0]$ direction (perpendicular to the drawing plane). The extension of the (2×3) unit cell in [001] direction is indicated by vertical lines. Using the C_{2V} symmetry of the surface, we labeled the inequivalent atoms per unit cell *A*(*B*) and *C*(*D*) for the first and second layer, respectively.

ing these uncertainties in mind, the errors for lateral shifts are estimated to be ±0.10 Å. We also calculated the influence of adsorbed nitrogen on the shadowing of Cu atoms beneath. Due to the larger vibrational amplitude of N (for a given force constant, the mean-square vibrational amplitude is inversely proportional to the mass), it changes the surface yield only insignificantly, even when adsorbed directly on top of a substrate atom.

As can be seen in Fig. 4, the lateral displacement of the third-layer atoms also changes their positions relative to the first-layer atoms *A*, which enables us to determine the direction of the displacement. Only for a lateral shift away from atom *A* does the third-layer atom remain unshadowed and causes an increase in backscattering yield. A detailed calculation with the first two atoms in a row displaced in opposite directions confirmed this analysis. From our measurements, we cannot determine the direction of the shifts for atoms *C*, but lateral atomic displacements away from atoms *B* and towards *D* seem the most likely. We note that by reanalyzing the x-ray data in Ref. 6, a slightly lower *R*-factor value was obtained for such a subsurface displacement pattern.[18] If we introduce lateral displacements into the missing-row models, it is only possible to make them fit our measured surface yields by including atomic displacements larger than 0.3 Å throughout the first three to four layers. This seems physically unreasonable and thus we rule out these models.

In the additional-row model proposed by Baddorf *et al.*,[6] large vertical buckling within the second and third layers was found. To corroborate this, we also measured the surface yield along the [101] crystallographic axis. The [101] direction is tilted by 54° relative to [110] and, therefore, is more sensitive to vertical atomic displacements. In the additional-row model there are six [101] atom rows in the (2×3) unit cell, all with the top atom in the second layer. We measured a yield increase of 2.4 atoms/row at an ion energy of 1.0 MeV. From that value, about 1.6 atoms/row are due to scattering from the reconstructed top layer and to flux focusing onto subsurface atoms. The additional 0.8 atoms/row show, that vertical displacements are important for subsurface layers, qualitatively confirming the x-ray scattering results.[6] Due to the complexity of the atomic arrangement along this direction, we did not attempt any quantitative evaluation of the vertical relaxations.

In summary, we have shown with single-alignment HEIS that the nitrogen-covered Cu(110) surface is reconstructed according to an additional-row model,[6] where the density of Cu atoms in the first layer is increased to $\frac{4}{3}$ ML. This leads to lateral displacements in the first layer larger than 0.3 Å. It also causes rearrangements in subsurface layers. Second-layer atoms (labeled *C* in Fig. 4) are shifted laterally by 0.30 Å and third-layer atoms (beneath atoms *A*) are displaced by about 0.07 Å. In addition, vertical displacements of atoms in the second and third layers were found in agreement with a recent x-ray scattering study.[6]

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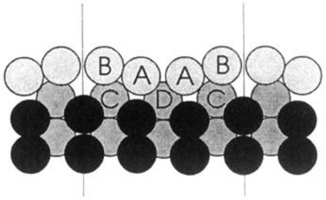

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