Surface structure determination of the \((2 \times 1)\)O–Cu(110) reconstruction by low-energy ion scattering

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Using impact collision ion scattering we show, that the reconstruction of the \((2 \times 1)\)O–Cu(110) surface is of the missing-row type where every other [001] row of copper atoms is missing. The oxygen atoms are located \(0.08 \pm 0.15 \text{ Å}\) below the copper atoms of the remaining rows. The second layer copper atoms are shifted laterally \(0.12 \pm 0.07 \text{ Å}\) away from the oxygen atoms in a pairing-row type reconstruction. The first layer is relaxed outward over \(0.23 \pm 0.04 \text{ Å}\) compared to the ideal spacing, whereas the distance between the second and third layer remains unchanged. A critical comparison of our results with the data available in the literature shows that the position of copper and oxygen atoms can be determined with an accuracy of about 0.05 and 0.15 Å, respectively.

1. Introduction

The oxygen induced \((2 \times 1)\) reconstruction of the Cu(110) surface has attracted much interest in the past as an intermediate step in the oxidation of a copper surface. In spite of a variety of studies there is still an ongoing controversy about the nature of the substrate reconstruction as well as about the vertical oxygen position. Recent investigations with LEED [1,2], low-energy ion scattering [3–6], SEXAFS [7,8], helicon incidence X-ray diffraction [9], and calculations based on effective medium theory [11] suggest that the reconstruction is of the missing-row (MR) type with every other [001] row of first-layer copper atoms missing. In contrast measurements with high-energy ion scattering [12], angle resolved photoemission [13], glancing incidence X-ray diffraction [14], and band structure calculations [15] favour the buckling-row (BR) reconstruction mechanism. In that case every second [001] copper row in the first layer is displaced vertically. Other reconstruction models have been tried with little success [1,4,6–8]. One of the main objections against the MR model, the large mass transport of half a monolayer involved in its growth, has been removed recently [16–19] by observing the growth of \((2 \times 1)\) reconstructed areas on top of the clean surface.

All studies agree that the oxygen atoms adsorb in the long-bridge sites of every other [001] copper-row. The actual vertical position is still under debate. The oxygen is either placed slightly above [1,2] or below [6,10] the first copper layer. From measurements of the Cu–O bond length [7,8,21] it was concluded that the adsorbate is located above the surface. However these studies did not consider the possibility of layer relaxations or subsurface reconstruction which indeed seem to occur [1,2,5,6,10].

The purpose of this paper is to distinguish between the two competing reconstruction models and to determine the actual surface geometry of the \((2 \times 1)\)O–Cu(110) system. The method used is the impact-collision ion scattering spectroscopy (ICISS). ICISS is an extremely surface sensitive technique and exploits the shadow cone which develops behind surface atoms when they are hit by an ion beam. The short range atomic order can then unambiguously be determined from measure-
ments only without much computational effort by triangulating the shadowing on surface atoms along various surface directions [20].

The paper is organized as follows. In the following two sections the experimental setup and the ICISS technique will be described briefly. The \((2 \times 1)O\) reconstruction and the oxygen position will be studied in sections 4 and 5. Finally, the obtained structure parameters will be compared to other results available in the literature in section 6.

2. Experiment

Our experimental setup has been described previously [20]. The noble-gas ion beam with energies up to 5 keV was produced in a differentially pumped ion source which allowed ion currents at the sample typically between 0.1 and 1.0 nA. The ion doses were low enough so that no beam damage could be observed during measurements. Charge exchange neutrals from the ion source were deflected at the last aperture before the sample by a bent of 5° in the beam line. The ion path was corrected by deflection plates which were also used for chopping the ion beam during time-of-flight (TOF) measurements. The angular width of the ion beam is determined by the apertures of the differential pumping stage to about ±1.0°.

Backscattered ions could be detected with a rotatable hemispherical energy analyzer allowing scattering angles between 0° and 160°. In addition, detection of backscattered ions and neutrals was possible with micro-channel-plates at a fixed scattering angle of 157°. The energy of these particles was determined with a TOF technique. The ion beam was chopped into bunches of typically 150 ns length. The length of the flight path from chopper to the sample was 0.35 m and from the sample to the detector 0.59 m. With each bunch a 40 MHz counter was started and stopped again by the first particle reaching the detector. The content of the counter was read out by a computer and is a direct measure of the flight time. All slower particles reaching the detector were ignored. The probability of such events was less than 0.2% at the given experimental conditions. To separate scattered ions and neutrals the charged particles could be accelerated in a drift tube of 0.5 m length between sample and detector. The detector was usually operated by applying a voltage of −2 keV to the “front” side facing the sample which simplified further signal processing. This mode caused an enhanced detection probability of ions compared to neutrals by a factor of 1.5.

The sample was mounted on a computer-controlled three-axis manipulator [22] and could be aligned relative to the ion beam for the ion scattering measurements better than 0.5°. It was cleaned by repeated cycles of argon ion bombardment and annealing to 800 K until no surface contamination could be detected with ion scattering spectroscopy (ISS) and the surface exhibited a well ordered LEED pattern. The surface order was also checked by ICISS measurements itself. Measurements on the \((2 \times 1)O\) structure were carried out after oxygen exposures of 20 L (1 L = 1.33 \times 10^{-4} \text{ Pa} \cdot \text{s}).

3. The ICISS method

In ICISS particles elastically backscattered from surface atoms are detected as a function of the incidence angle of the ion beam relative to the sample surface. Scattering angles near 180° are used to assure that the projectiles have undergone one almost head-on collision with the target atoms. If only backscattered ions are detected trajectory dependent neutralization can obscure ICISS measurements [6,20]. We therefore detected also backscattered neutral particles. A typical TOF distribution of \(^{20}\text{Ne}\) ions and neutrals backscattered from the clean Cu(110) surface is shown in fig. 1. The ion beam of 5 keV energy was incident along the [112] direction at an angle of 55°. Ions and neutral particles were separated in the drift tube by applying a voltage of −2.5 keV. The corresponding quasi-single scattering peaks can be seen at flight times of 5 and 6.6 µs respectively. Both peaks are located on a broad background due to multiple scattered particles out of the deeper layers [24] and at short flight times also due to photons emitted by particles hitting the front side of the drift tube. The background was
Fig. 1. Typical time-of-flight distribution for a 5 keV Ne+ ion beam at an incidence angle of 55°. Elastically scattered ions and neutrals can be seen at flight times of 5.0 and 6.6 μs respectively. For further data processing a parabolic background (lines) is subtracted in the vicinity of both peaks.

taken into account by the solid lines indicated in fig. 1 which correspond to parabolic fits through the data points adjacent to the quasi-single scattering peaks. For comparing the intensity of ion and neutral peak the ion yield has to be reduced by a factor 5.7 taking into account an increased acceptance angle caused by the ion acceleration in the drift tube and, as mentioned earlier, the enhanced detection probability for ions. The correction leads to an ion yield of about 50% as shown in fig. 3 where ICISS spectra of ions and neutral particles are shown along the [112] azimuth of the clean and reconstructed surface. This surprisingly high value agrees well with experiments in ref. [6] and can be explained by the occurrence of reionization processes during the violent large angle collision [20]. With other projectiles like helium no such ionization can be found and the backscattering yield is dominated by neutral particles.

For determining the atomic geometry we make use of the shadow cone behind the target atoms where no projectiles penetrate. During the ICISS angular scan the shadow cone is swept across neighbor atoms. The angle of incidence where the atoms emerge out of the shadows of their neighbors is characterized by a sharp rise in the backscattering signal which is even enhanced due to focussing of projectile trajectories at the shadow cone [20]. This can be seen in fig. 3 where ICISS spectra obtained along the [112] azimuth of the clean and reconstructed surface are shown. The number of quasi-single scattered ions (lines) and neutral particles (lines and dots) is plotted versus the angle of incidence Ψ relative to the sample surface. The energy position of both peaks did not change with Ψ indicating that only quasi-single scattering occurs. The steepness of the slope is attenuated by thermal vibrations of the surface atoms [23]. A critical angle Ψc is then defined at 50% of the slope height. From measurements of the critical angle Ψc the interatomic distance d can be calculated using the known shadow cone.

The shadow cone itself was calibrated on the well known Cu(110) surfaces [6]. Fig. 2 displays the arrangement of surface atoms in the first layer (filled circles) and the second layer (grey circles). Along the indicated surface directions ICISS spectra were measured. Table 1 shows a compilation of the obtained experimental critical angles Ψc

Figure 2. Schematic view on the clean Cu(110) surface. Copper atoms in the first layer (large filled circles) and in the second layer (grey circles) are shown.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Experimental Ψc (deg)</th>
<th>Theoretical Ψc (deg)</th>
<th>Experimental d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[110]</td>
<td>17.0</td>
<td>17.0</td>
<td>2.55</td>
</tr>
<tr>
<td>[001]</td>
<td>13.1</td>
<td>13.2</td>
<td>3.61</td>
</tr>
<tr>
<td>[112]</td>
<td>11.1</td>
<td>11.4</td>
<td>4.42</td>
</tr>
<tr>
<td>[111]</td>
<td>8.5</td>
<td>8.9</td>
<td>6.25</td>
</tr>
<tr>
<td>[332]</td>
<td>7.4</td>
<td>7.1</td>
<td>8.47</td>
</tr>
</tbody>
</table>

a) The experimental and calculated critical angles along the indicated directions are shown. Calculations were performed for an optimized potential with screening parameters of 0.77 ± 0.03 for neon and 0.67 ± 0.03 for helium projectiles. In addition the nearest neighbor distance of the copper atoms is given for the different surface directions.
of first layer shadowing for the scattering of 5 keV \textsuperscript{20}Ne and 600 eV \textsuperscript{3}He. From the known interatomic distances \( d \) included in table 1 we calculated the expected critical angles \( \psi_c^{th} \) with [20]

\[
\psi_c^{th} = \psi_c^0 + \Delta \psi_c
\]

where \( \psi_c^0 \) is the critical angle for nonvibrating atoms obtained from the projectile-target interaction potential with a screening length reduced by an adjustable factor \( \xi \) [20]. The effects of thermal atom vibrations on the critical angle \( \psi_c^0 \) can be described satisfactorily by a shift \( \Delta \psi_c \) to lower angles of incidence which depends merely on the sample temperature and the Debye-temperature of the vibrating atoms [20]. In the case of Cu(110) first layer atoms vibrate at room temperature according to a Debye-temperature of 224 K [23,26] which is in agreement with literature values [27]. This vibrational behavior does not change upon oxygen adsorption [25]. Table 1 shows also the optimized values of \( \psi_c^{th} \) corresponding to screening factors of 0.77 \( \pm 0.03 \) for 5 keV \textsuperscript{20}Ne and of 0.67 \( \pm 0.03 \) for 0.6 keV \textsuperscript{3}He. The errors were calculated for the uncertainties in determining \( \psi_c \) of 0.5\( ^\circ \) (1.0\( ^\circ \)) for neon (helium). The good agreement between the experimental and calculated critical angles for all distances \( d \) shows that the influence of neighboring matrix atoms on the trajectories are negligible. The finite size of the sample and the ion beam changes slightly the shape of the spectra [23] but seems to have little influence on the critical angle.

The now calibrated shadow cone can be checked by determining the distance between the first two layers of the clean surface from the shadowing of second layer atoms. In the right part of fig. 3 the atomic geometry in the scattering plane is indicated together with the projectile trajectories at the shadowing critical angles \( \psi_c \). The calculated values of \( \psi_c \) are marked in the spectra by arrows. From the critical angle (B) at 46\( ^\circ \) \( \pm 0.5\)\( ^\circ \) in fig. 3 we deduce a contraction of the first two layers spacing of 0.06 \( \pm 0.03 \) Å compared to the ideal layer distance. This value is in good agreement with the literature [6]. To describe the vibrations of second layer atoms a Debye-temperature of 286 K was used resulting from surface phonon calculations [26]. However by using the first layer value

Fig. 3. ICISS spectra of backscattered ions (lines) and neutrals (lines and dots) on the clean (top) and oxygen covered (bottom) surface along the [112] azimuth. On the right hand side cuts perpendicular to the surface in [112] direction are shown schematically for the clean surface and the reconstructed surface according to the missing and buckling row models. The expected shadows are shown as trajectories at the critical angles. The calculated critical angles are indicated in the spectra by arrows.

or the bulk value of 343 K the deviations in \( \psi_c \) are about 0.1\( ^\circ \) each and therefore negligible.

4. Substrate reconstruction of the \((2 \times 1)O\) structure

4.1. The \([1\overline{1}2]\) azimuth

In the bottom part of fig. 3 ICISS spectra of the oxygen covered surface in the [112] azimuth are shown. Instead of the first layer shadowing (A) two new structures appear at critical angles of 6.9\( ^\circ \) and 21.3\( ^\circ \). We identify the critical angle at 6.9\( ^\circ \) with the new first layer shadowing (a). The interatomic distance is twice that of the clean surface. The same behavior was found along the [110] and [332] azimuths but not along the [1\overline{1}1] and [001] azimuths. The critical angles of the \((2 \times 1)O\) structure in these surface directions are listed in table 2. Considering the surface geometry shown in fig. 2 this proves clearly that every other [001] row of copper atoms has to be modified in
Table 2
Measured critical angles on the reconstructed surface compared to the values predicted by the BR and MR models a)

<table>
<thead>
<tr>
<th></th>
<th>( \psi_{\text{exp}} )</th>
<th>( \psi_{\text{MR}} )</th>
<th>( \psi_{\text{BR}} )</th>
<th>( \psi_{\text{Oxygen}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[110]</td>
<td>10.3 ± 0.5</td>
<td>10.3</td>
<td>19.5</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td>20.5 ± 1.5</td>
<td>21.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.0 ± 1.5</td>
<td>27.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.5 ± 1.0</td>
<td>33.0</td>
<td>31.2</td>
<td>31.2</td>
</tr>
<tr>
<td></td>
<td>38.0 ± 1.5</td>
<td>38.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61.0 ± 1.5</td>
<td>60.3</td>
<td>61.8</td>
<td>61.8</td>
</tr>
<tr>
<td>[332]</td>
<td>5.5 ± 1.0</td>
<td>4.3</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.0 ± 1.0</td>
<td>31.4</td>
<td>30.2</td>
<td>30.2</td>
</tr>
<tr>
<td></td>
<td>50.0 ± 1.5</td>
<td></td>
<td>49.8 ( \text{zz} )</td>
<td></td>
</tr>
<tr>
<td>[11\bar{1}]</td>
<td>8.5 ± 0.5</td>
<td>8.9</td>
<td>8.9</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>50.5 ± 1.5</td>
<td></td>
<td>50.7</td>
<td></td>
</tr>
<tr>
<td>[1\bar{1}2]</td>
<td>6.9 ± 0.5</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>21.3 ± 0.8</td>
<td>21.3</td>
<td>21.0</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>49.0 ± 1.5</td>
<td>49.3</td>
<td>49.7</td>
<td>49.7</td>
</tr>
<tr>
<td>[001]</td>
<td>13.6 ± 0.5</td>
<td>13.2</td>
<td>13.2</td>
<td>14.0</td>
</tr>
</tbody>
</table>

a) The critical angles of the oxygen shadows were calculated for an oxygen-neon potential with \( \xi = 0.68 \). This value was obtained by calibrating the oxygen shadow cone with oxygen adsorbed in long bridge sites 0.08 Å below the first layer. Critical angles caused by zig-zag scattering are marked with \( \text{zz} \).

In order to allow the observed next-nearest neighbor shadowing. This can be done by either displacing the rows vertically in the BR model or by removing them totally from the surface in the MR model. The predicted critical angles of the two reconstruction models are included in table 2. Both models yield the same first layer shadows. By considering the additional shadowing features we can, however, discriminate between the models. In the [112] azimuth the essential structure parameters for both models can be determined. Since the interaction potential is weaker for oxygen atoms, we assume, that shadows are mainly cast by copper atoms. In section 5 also oxygen shadows will be identified.

The 3° shift of the critical angle at 46.0° to higher incidence angles indicates an outward relaxation of the first layer. In the BR model this shift can be determined from the critical angle (β). In the MR case this is accomplished using shadow (d). The feature at 49.0° is a mixture of two shadows (b) and (c). For both models a vertical distance between the first two layers of 1.5 Å can be deduced. While for the MR model all shadows observed experimentally can be reproduced now, the position of the other [001] rows has to be determined in the BR model. For a vertical distance of 0.76 Å between the buckled [001] rows the shadow (δ) is in good agreement with the experimental value of 21.3°. That determines also the shadow (γ). At the deduced critical angle of 37.0° no shadowing can be observed in the ICISS spectra. The same problem arises if the shadow (γ) is used to fit the critical angle at 49.0° as was done in ref. [4]. This would leave critical angle (δ) unobserved. Together with the data presented in the next section we, therefore, can exclude the BR model.

4.2. The [11\bar{1}] azimuth

Similar discrepancies were found along the [110] surface direction as can be seen in fig. 4 where ICISS spectra in this direction and the possible trajectories predicted by the two reconstruction models are shown. The spectra taken at scattering angles of 130°, 140°, and 160° show backscattered ions detected with the rotatable analyzer whereas the spectra at scattering angles of 157° consist of backscattered neutral particles. For reference a neutral particle ICISS spectrum of the clean surface is shown at the bottom of fig. 4. The first layer shadows are reproduced by both models (trajectory (a) in the MR and trajectory (α) in the BR model). At larger angles of incidence a variety of new structures due to shadowing of subsurface atoms are seen. ICISS spectra in the [110] azimuth are composed of shadows cast by atoms in the first two layers. From the analysis of the [112] direction we know that the second layer exhibits no major reconstruction compared to the first layer of an unreconstructed surface. In consequence, no shadows on subsurface atoms cast by second layer atoms can be seen as on the clean surface. Therefore the structures at higher incidence angles in fig. 4 must be due to shadowing of the first layer atoms onto those in the third layer.
In the BR model the first layer is equally close packed as on the clean surface and in this case shadows on subsurface atoms should also not be observed. Besides the first layer shadowing ($\alpha$) only one further critical angle ($\beta$) can occur. The MR model can explain more of the experimentally observed structures in this azimuth. In addition the changes in the ICISS spectra with varying incidence angle can be explained by the trajectories (a)–(d) of the MR model. The sharp decrease at higher incidence angles of the focussing peaks with critical angles (e) and (c) indicates blocking of projectiles by first layer atoms. Of both structures only the shadow (c) at 38.0° is seen in the spectra of backscattered ions at a scattering angle of $\theta = 160°$. The structure disappears with decreasing scattering angle which proves blocking of scattered particles by first layer atoms. For $\theta = 140°$ also the shadow (e) at $\psi_c = 20.5°$ is visible, whereas at larger scattering angles neutralization of projectile ions on the outgoing path probably causes this structure to disappear. Due to neutralization both focussing peaks are more intense in spectra of scattered neutrals making backscattering from subsurface layers plausible. At $\theta = 130°$ a new shadow (d) is fully developed which can be seen at larger scattering angles due to first layer blocking only as a broadening of the slope of another shadow at a critical angle of $\psi_c = 31.5°$. This last structure cannot be explained within any of the reconstruction models and is most likely to be identified as an oxygen shadow ($b'$) on the second copper layer (see section 5). In addition, a shadow (b) onto the third layer is visible at all scattering angles $\theta$. Considering all critical angles in the [112] and [110] direction we have to exclude the BR model which can explain only five out of nine measured shadows and leaves one predicted critical angle unobserved in experiment. The MR model on the contrary explains all observed critical angles except one which, however, is due to a shadow cast by oxygen atoms and also describes the variation of the shadowing structures with the scattering angle correctly.

In the [110] azimuth we can now deduce the distance between the first and third layer by the critical angles (b), (c), (d), and (e). The peaked shapes of trajectories (c) and (e) indicate blocking at larger incidence angles which might influence the calculated critical angles. Trajectory (b) coincides with a further oxygen shadow ($a'$). Considering these limitations we determine a distance between the first and the third layer of 2.79 Å with an estimated uncertainty of about ±0.2 Å. Because of the large experimental error we are not able to determine a lateral shift or a vertical buckling of third layer atoms.

### 4.3. Second layer reconstruction

In general a possible reconstruction of the second copper layer consists of lateral and vertical shifts of the two atoms in the unit cell. The geometry of the reconstructed surface is shown in fig. 5. The large and small full circles indicate copper atoms in the first and third layer, respectively, whereas the grey circles denote second layer...
atoms. Any lateral or vertical shifts resulting in a loss of the [001] or [110] mirror plane would cause surface domains. A domain structure is difficult to resolve with ICISS and would merely broaden the slope at the corresponding critical angles. For shadowing on second layer atoms along the [112] azimuth (trajectory d in fig. 3) no broadening is detected compared to the first layer shadow (a) in fig. 3. In both cases the interatomic distances are almost equal resulting in identical slope widths at the corresponding critical angles. We are then left with a possible lateral shift of the two second layer atoms in opposite directions as has been reported recently [1,2,10].

For determining such a shift we can use the following effect. If the line connecting shadowing and shadowed atom is not within the scattering plane, the incoming projectiles can reach the shadowed atom at lower incidence angles. For such zig-zag shadowing the critical angle is always smaller than for conventional shadowing. If we vary now the angle relative to the scattering plane i.e. the azimuthal angle, a maximum of the critical angle of the corresponding ICISS spectra indicates the position with both atoms in the scattering plane. This was done in the vicinity of the [112] azimuth for critical angles of first and second layer shadowing trajectories (a) and (d) of fig. 3 respectively. The result is shown in fig. 6 together with identical measurements in the [112] azimuth. The difference between the observed maxima for first layer shadowing (bottom part of fig. 6) of 70.5° is identical with the ideally expected value

and was also obtained on the clean surface. In contrast, the difference value of the second layer shadowing is only 68.8°. A subtraction of the background observed in these measurements would make this value even smaller. An influence of the adsorbed oxygen sitting in [001] long bridge sites (see section 5) can be ruled out. In this case a possible deflection of the incoming particles would be smaller than 0.5°. The measurements show clearly a row pairing of the second layer atoms towards the missing first layer copper rows by a distance of 0.12 ± 0.07 Å. With this lateral shift we can now reinvestigate the distance between the first two layers. From second layer shadows in the [112] direction at 21.3° ± 0.8° and the [332] direction at 31.0° ± 1.0° we deduce a value of 1.51 ± 0.04 Å.

Fig. 5. Schematic view on the (2×1) reconstructed Cu(110) surface. Copper atoms in the first layer (large filled circles), in the second layer (grey circles), and in the third layer (small filled circles) are shown. Oxygen atoms are indicated as open circles. 

5. The oxygen position

There is agreement in the literature that adsorbed oxygen occupies the [001] long bridge site. Oxygen atoms can also cast shadows on neighboring atoms as copper atoms do. The absence of any such additional shadows in the [001] direction besides the first layer Cu–Cu shadowing proves the long bridge position being the correct adsorp-
tion site. Furthermore, the experimentally observed small shift of the first-layer shadowing of 0.5° ± 0.3° compared to the clean surface can be explained by subsurface oxygen. From Monte Carlo simulations of the ICISS spectra [23] calculating the scattering by an Cu–O–Cu chain we find a shift of about 1° for the first layer shadowing induced by oxygen adsorbed roughly 0.1 Å below the copper atoms. In this calculation we assumed equal screening parameters ξ = 0.77 for the copper and oxygen potentials and chose the vibration amplitude equal to that of the copper atoms [25]. We cannot, however, exclude the possibility that the observed shift may be caused by scattering from subsurface layers along the very open [001] azimuth.

Oxygen adsorption in [001] long bridge sites slightly below the first layer explains all additional critical angles in table 2. For the [110] azimuth all possible trajectories at the observed critical angles for a shadowing of oxygen atoms in long bridge sites on second layer copper atoms are shown in fig. 4. Since no shadowing of the unreconstructed [110] second-layer copper chains is observed, the oxygen must sit somewhere above these chains blocking the corresponding trajectories. The shadow (b') explains the critical angle at 31.5° whereas shadow (a') coincides with shadow (b) of substrate atoms. Projectiles following trajectory (c') are blocked by oxygen atoms after the head-on collision with second-layer copper atoms. Therefore, the corresponding focussing peak cannot be observed unless the (2 × 1) oxygen structure is partly damaged which was only found to occur by ion induced desorption of oxygen atoms at temperatures above 800 K. In the [111] and [332] azimuths the critical angles at 50.5° and 50.0° are due to shadowing on third layer copper atoms. For the [332] direction this can only be accomplished by zig-zag scattering out of the scattering plane.

From the shadowing behavior of oxygen on copper atoms it is possible to determine the exact vertical oxygen position since the oxygen shadow cone is unknown. This problem can be solved by detecting lighter projectiles like helium backscattered from the oxygen atoms. In this case we are able to calibrate the shadow cone as described in section 3. Because of the high neutralization probability of helium ions it is necessary to detect the backscattered neutrals. One problem arises then from a high background due to multiple scattered projectiles out of the bulk region. Like in high energy ion scattering we are with this method only surface sensitive along bulk channeling or blocking directions or at small angles of incidence [24]. Considering the just mentioned difficulties we choose the [221] azimuth to determine the vertical oxygen position. In this direction shadowing of first layer copper atoms on the oxygen adsorbed in long bridge sites occurs. The measured TOF distributions of backscattered particles for a 600 eV 3He ion beam impinging on the oxygen covered surface are shown in fig. 7 for various incidence angles. The low ion energy was chosen to increase the scattering cross section for oxygen and to reduce the penetration depth of the ion beam. We used the lighter helium isotope since the detection probability of the micro-channel plates is higher for larger energies of the backscattered particles.

At flight times of about 6 μs a peak is visible due to projectiles elastically scattered from oxygen atoms. This peak is superposed on a broad inelastic background which was corrected by parabolic
fits also shown in fig. 7 as solid lines. The integrated oxygen backscattering signal versus the incidence angle is shown in the insert. We deduce a critical angle of $12.0^\circ \pm 1.0^\circ$. Using the screening parameter from table 1 and equal vibration amplitudes for copper and oxygen [25] the experimental critical angle for oxygen positioned within the first copper layer is calculated to be $11.2^\circ$. From the difference of both critical angles the oxygen position is determined to be $0.08 \pm 0.15 \text{Å}$ below the first copper layer. The error includes the uncertainty in the oxygen vibration amplitude.

6. Summary and conclusions

We have shown that the $(2 \times 1)\text{O-Cu}(110)$ surface shows a first-layer reconstruction according to the MR model. The layer distance $d_{12}$ is modified compared to the bulk value and the second-layer atoms show a pairing-row like shift $\Delta$ in [110] direction towards the missing first-layer rows. The oxygen was found to absorb in [001] long bridge sites at a vertical distance $d_{\text{oxygen}}$ relative to the first-layer copper atoms resulting in Cu-O rows in [001] direction. Studies of the growth mechanism showed that the growth of the $(2 \times 1)\text{O}$ structure proceeds via “added [001] rows” of copper and oxygen atoms on top of the unreconstructed surface [16–19]. The present paper is the first ICISS study which succeeded in determining the complete geometry of the surface structure with four parameters. We have summarized our results in table 3, where we compare the most recent studies of the $(2 \times 1)\text{O-Cu}(110)$ surface. We have included only work which gave more than one distance and which found the missing row reconstruction. For a comparison with the SEXAFS [7,8] and X-ray photoelectron diffraction [21] (XPD) results we included two additional columns in table 3 for the distances of the oxygen atoms to the nearest neighbor ($R_1$) in the top layer and to the next nearest neighbor ($R_2$) in the second layer. Our results agree well with the data of van de Riet et al. [6]. The discrepancy in $R_2$ comes from the neglect of the shift $\Delta$ in the second layer by these authors. The X-ray diffraction data by Feidenhansl et al. [10] give a large first layer relaxation and an oxygen position 0.34 Å below the first layer which leads to a next nearest neighbor distance considerably smaller than in any other work. There are two LEED [1,2] studies which agree quite well with each other except for the lateral shift $\Delta$. The difference of 0.07 Å is, however, within the error limits. We mention here that both studies include a buckling of the third layer of 0.07 Å [1] and 0.02 Å [2]. Wever et al. [2] determine also the distance between the third and the fourth layer to be 1.29 Å. Within the error limits the buckling of the third layer and the

<table>
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<tr>
<th></th>
<th>$d_{12}$ (Å)</th>
<th>$d_{23}$ (Å)</th>
<th>$\Delta$ (Å)</th>
<th>$d_{\text{oxygen}}$ (Å)</th>
<th>$R_1$ (Å)</th>
<th>$R_2$ (Å)</th>
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<td>ICISS [5]</td>
<td>1.60 ± 0.13</td>
<td>1.15 ± 0.06</td>
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<td>−0.10 ± 0.10</td>
<td>1.81 ± 0.01</td>
<td>1.90 ± 0.10</td>
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<td>ICISS [6]</td>
<td>1.51 ± 0.04</td>
<td></td>
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<td>−0.08 ± 0.15</td>
<td>1.81 ± 0.01</td>
<td>2.00 ± 0.14</td>
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<tr>
<td>This work</td>
<td>1.51 ± 0.04</td>
<td>1.28 ± 0.20</td>
<td>0.12 ± 0.07</td>
<td>1.81 ± 0.01</td>
<td>2.00 ± 0.14</td>
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<td>X-ray dif-</td>
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<td>0.031 ± 0.005</td>
<td>−0.34 ± 0.17</td>
<td>1.84 ± 0.06</td>
<td>1.85 ± 0.16</td>
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<td>fraction [10]</td>
<td>1.49 ± 0.03</td>
<td>1.21 ± 0.03</td>
<td>0.03 ± 0.03</td>
<td>0.04 ± 0.03</td>
<td>1.81 ± 0.01</td>
<td>2.01 ± 0.05</td>
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<td>LEED [1]</td>
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<td>1.81 ± 0.01</td>
<td>2.05 ± 0.12</td>
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<td>SEXAFS [8]</td>
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<td>XPD [21]</td>
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Table 3
The structural parameters of the $(2 \times 1)\text{O-Cu}(110)$ surface compared to the literature

a) Listed are the vertical distances $d$ of the corresponding layers, the lateral shift $\Delta$ of the second-layer atoms towards the missing first-layer rows, the vertical oxygen position relative to the first layer and the distance to the nearest ($R_1$) and next-nearest copper-neighbors of the oxygen atoms. Mean values and standard deviations were calculated for each parameter individually.
relaxation between the third and fourth layer are identical to the bulk geometry.

In order to get a feeling of how well the geometry of (2 x 1)O–Cu(110) surface structure is known, we simply calculated in each column the mean values and the corresponding standard deviations. In this procedure we weighted all data equally irrespective of the quoted errors of the individual measurements. The agreement on the position of copper atoms is about 0.05 Å, whereas the uncertainty in the oxygen position is 0.15 Å. The small error in the nearest neighbor distance $R_1$ is due to the long bridge site for oxygen, which makes $R_1$ almost independent of the vertical oxygen position. The agreement of the mean values of $R_1$ and $R_2$ with the bond length measurements [7,8,21] is very good. It could be even improved, if we would discard the X-ray diffraction results. X-ray diffraction has some problems in determining the position of a light scatterer like oxygen perpendicular to the surface.

The current state of the surface structure determination in a $3.6 \times 5.1$ Å$^2$ unit cell with four inequivalent atoms and four structure parameters is an accuracy of 0.05 for heavy and 0.15 Å for light atoms. The limitations in the accuracy of ICISS measurements are given by the sharpness of the shadows which depend mainly on the vibrational behavior of the surface atoms. For X-ray and low-energy electron diffraction the limits in the accuracy are ultimately set by the coherence length of the probe and the order of the surface phase. It is going to be interesting whether the accuracy can be improved in the future.

Acknowledgements

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References