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Low-energy electron-diffraction crystallographic determination for the Cu(110)2×1-O surface structure

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A multiple-scattering analysis of low-energy electron-diffraction intensities has been made for the Cu(110)2×1-O surface structure, a system for which different techniques have recently been providing very different conclusions regarding both the nature of the reconstruction of the copper structure and the height that the O atoms are held above (or below) the topmost Cu layer. The analysis here used nine diffracted beams at normal incidence, and it confirms the missing-row model for this surface. We find that the O atoms are held around 0.04 Å above the Cu atoms, while the first-to-second and second-to-third Cu-Cu interlayer spacings are expanded by 16% and contracted by 5%, respectively, from the bulk value. There is a vertical buckling in the third Cu layer by about 0.07 Å, and a possibly slight lateral relaxation (magnitude 0.03 Å) in the second copper layer.

The reconstructions and relaxations that may be induced in metal surfaces of low-index orientation in the presence of submonolayer coverages of chemisorbed oxygen can provide a significant challenge in surface science. One particular case concerns the structure formed by a half-monolayer coverage of O on the (110) surface of copper, for which low-energy electron diffraction (LEED) shows a (2×1) translational symmetry.[1] Many studies with a wide range of techniques agreed that the O atoms chemisorb on long-bridge sites (i.e., sites of twofold coordination along the [001] direction which bridge pairs of Cu atoms in adjacent rows parallel to $[1\bar{1}0]$),[2-10] although the height of O relative to the topmost Cu layer has varied very widely. Early work with low-energy-ion scattering (LEIS) indicated that O was up to 0.6 Å below the Cu layer,[2] although more recent analyses range from 0.35 Å above by surface extended x-ray-absorption fine structure[6,7] (SEXAFS) and near-edge x-ray-absorption fine structure[8] to 0.1 ± 0.1 Å below according to the latest LEIS study.[10] The situation is further confused regarding any reconstructions or relaxations that occur in the structure of copper in the vicinity of the chemisorbed O atoms. Some studies, for example, with LEIS,[2,10] impact-collision ion-scattering spectroscopy (ICISS),[4,11] He atom diffraction,[3] and SEXAFS,[7] have concluded that every other [001] row in the topmost Cu layer (specifically those adjacent to the O atoms) is missing. However, even within the missing-row (MR) model there are discrepancies; for example, the LEIS and ICISS analyses indicate substantial expansions in the first-to-second metal interlayer spacing,[10,11] whereas the SEXAFS analysis assumes this spacing holds at the bulk value. By contrast, studies with grazing-angle x-ray scattering,[12] angular-resolved photoemission spectroscopy,[5,9] and high-energy ion scattering[13] concluded that this surface structure fits the buckled-row (BR) model in which alternating top-layer Cu atoms along $[1\bar{1}0]$ have different heights above the second metal layer. Supporting the latter conclusion is the very recent analysis with scanning tunneling microscopy by Chua, Kuk, and Silverman[14] who reported that the vertical displacement in the alternating Cu rows is as much as 0.8 ± 0.2 Å, and that the O atoms are held below the topmost Cu atoms so that the O–Cu bond lengths approximate those both from the SEXAFS study and from the structure of bulk Cu_2O.[15] The contrasting structural details reported for this surface indicate that independent quantitative assessments are needed. Accordingly, we have undertaken a multiple-scattering LEED analysis, and that provides the subject of the present communication.

All experimental details closely follow those used in our earlier quantitative LEED study for the chemisorption of oxygen on the Cu(100) surface.[16] Briefly, the single-crystal sample was cut and polished to within 0.2° of the (110) plane, and after sufficient ion bombardment and annealing cycles inside the vacuum chamber the surface was shown to be clean by Auger electron spectroscopy and to give a sharp (1×1) LEED pattern. This surface was then exposed to reagent grade oxygen, and the optimal adsorption conditions were determined by measuring spot profiles for the half-order beams. The sharpest (2×1) LEED patterns were obtained with a 5-min exposure to oxygen at 4×10^{-8} Torr followed by a 5-min anneal at 100 °C. Intensity-versus-energy [$I(E)$] curves for normal incidence were recorded over the approximate energy range 50–250 eV for the nine diffracted beams designated (0,1), (1,1), (2,0), (2,1), $(0,\frac{1}{2})$, $(1,\frac{1}{2})$, $(0,\frac{3}{2})$, $(1,\frac{3}{2})$, and $(2,\frac{1}{2})$ using the beam notation defined by Zanazzi *et al.*[17] The details in the measurement procedures followed those given previously.[16,18]

The LEED multiple-scattering calculations in this analysis used standard procedures.[19,20] Briefly, the multiple scattering between atomic layers was calculated with the layer-doubling method, although composite layers were added with the combined-space formalism when small interlayer spacings were involved.[21] All nonstructural parameters were kept the same as those used in our recent study of O chemisorption on the (100) sur-

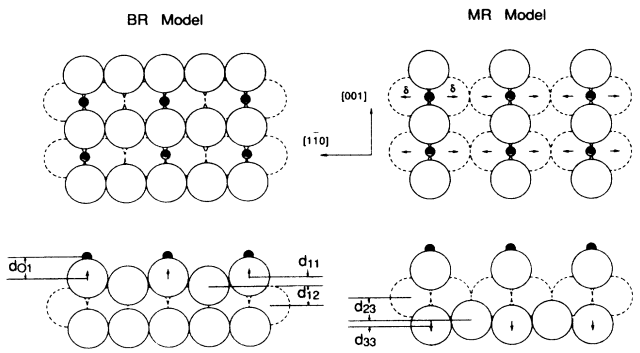

FIG. 1. The missing-row (MR) and buckled-row (BR) models for the Cu(110)2×1-O surface structure, where the O atoms are shown as small solid circles. The upper figures indicate views from the top, while the lower figures give corresponding views from the side. Atoms in the second Cu layer are shown by dashed circles. Positive values for the buckling parameters d_{11} and d_{33} for the first and third Cu layers, respectively, and for the lateral relaxation δ in the second Cu layer (MR model), correspond to displacements in the directions shown by the relevant arrows (negative values correspond to displacements in the opposite directions to those shown here). Where layer buckling is included, interlayer spacings are defined by the vertical separation between a bottom atom in the top layer and a top atom in the bottom layer.

face.[16,22] Emphasis was given here for the BR and MR models of the Cu(110)2×1-O surface although the nonreconstructed (NR) model was also included for comparison. The BR and MR models are illustrated in Fig. 1; the NR model corresponds to the BR model with no buckling in the first metal layer (i.e., $d_{11}=0.00$ Å where the geometrical parameters varied in the study are also included in Fig. 1). The measured $I(E)$ curves were compared in the first instance with those calculated for the models corresponding to the parameters given in Table I; the comparisons being made both by visual analysis and with the numerical many-beam reliability index R_{MZJ}. This index (or R factor) relates to that introduced by Zanazzi and Jona,[23] but in the modified version proposed by Van Hove and Koestner.[24] The objective of the calculations is to find the geometrical model which can give the best match to the experimental intensity curves, and correspondingly give the lowest value for the reliability index.

Results for the BR model show that the correspondence with the experimental $I(E)$ curves increases as the buckling parameter d_{11} in the calculations decreases; indeed

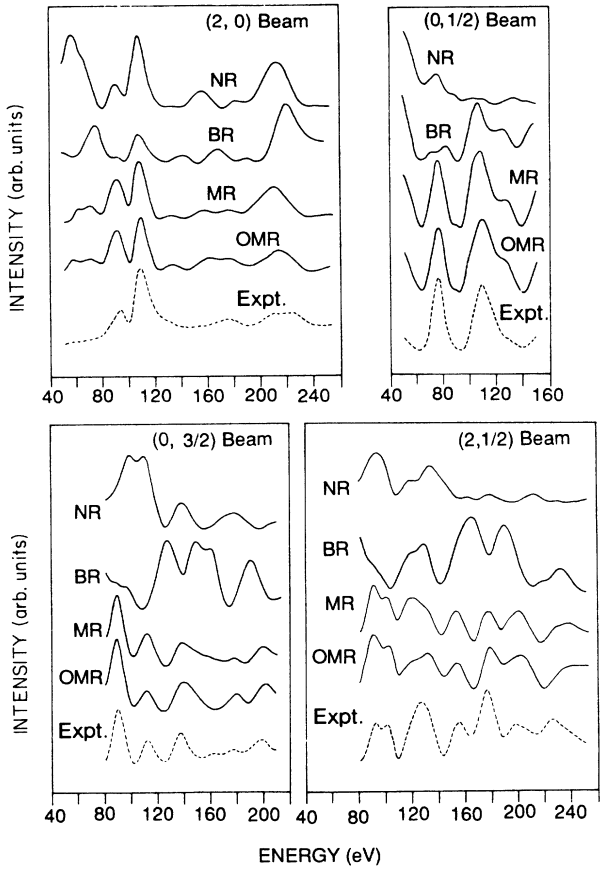

FIG. 2. $I(E)$ curves measured at normal incidence for the (2,0), $(0,\frac{1}{2})$, $(0,\frac{3}{2})$, and $(2,\frac{1}{2})$ beams (shown as dashed lines) from Cu(110)2×1-O and compared with calculated curves for the nonreconstructed (NR) model (with $d_{01}=0.00$, $d_{12}=1.36$ Å), the buckled-row (BR) model (with $d_{01}=-0.40$, $d_{11}=0.80$, $d_{12}=1.26$ Å), the missing-row (MR) model (with $d_{01}=0.00$, $d_{12}=1.49$ Å) and the optimized missing-row (OMR) model (optimized parameters specified in Table II).

the NR model appears favored relative to the BR model. The initial LEED results show further that (i) the optimal position of O is close to coplanar with the topmost Cu layer in both the NR and MR models, and (ii) the MR model gives a better correspondence with the experimental intensities than the NR model. Comparisons between experiment and calculation are shown in Fig. 2 for just four representative beams to save space, but three are fractional-order beams. The curves marked BR are

TABLE I. Ranges of parameter values (all in Å) included in the initial multiple scattering calculations for the missing-row (MR), buckled-row (BR), and nonreconstructed (NR) models of the Cu(110)2×1-O surface structure. Parameters for deeper layers are fixed at the values for bulk Cu.

MR	BR	NR
$d_{01}=-0.20$ (0.10) 0.40	$d_{01}=-0.40$ (0.20) 0.20	$d_{01}=-0.20$ (0.10) 0.10
$d_{12}=1.26$ (0.05) 1.61	$d_{11}=-0.80$, -0.60, -0.40, -0.15 0.15, 0.40, 0.60, 0.80	$d_{12}=1.26$ (0.05) 1.61
	$d_{12}=1.26$ (0.05) 1.61	

specifically for the model proposed by Chua *et al.*[14]; it seems clear that the LEED evidence does not support that model. In Fig. 2, NR and MR identify calculated curves for models where O is coplanar with the topmost Cu atoms and the spacing d_{12} is chosen for optimal correspondence with the experimental curves. At this stage for the MR model R_{MZJ} is 0.228 for the nine diffracted beams.

Following the conclusion from the initial analysis that the MR model provides a better account of the experimental $I(E)$ curves than the NR or BR models, the next step is to see how far the correspondence can be increased by considering further relaxations in the MR model, specifically for lateral relaxations parallel to the $[1\bar{1}0]$ direction in the second copper layer, and a buckling in the third copper layer. Table II reports the ranges of parameter values included in the further analysis, as well as the values that minimize R_{MZJ} according to a standard interpolation routine. The curves calculated for this model are marked optimized missing row (OMR) in Fig. 2, and for the nine beams R_{MZJ} is reduced to 0.196. The correspondence between experiment and calculation is at a good level for all diffracted beams; this indicates that the structure is basically correct, although a number of further refinements are still possible. These could include consideration of O asymmetrically placed with respect to the surface, as suggested for the corresponding surface of nickel both by a recent electron-energy-loss spectroscopy study[25] and by a preliminary LEED analysis.[26] The uncertainties for the optimal parameters quoted in Table II are estimated at ± 0.03 Å.

In summary we believe this LEED analysis has clarified some controversial details for the Cu(110)2×1-O surface structure. The new evidence supports the missing-row model with O atoms adsorbing in long-bridge sites while held close to, although probably slightly above, coplanarity with the topmost Cu atoms. This result is very close to the limits of uncertainty in the recent results from LEIS.[10] The first-to-second Cu-Cu interlayer spacing expands by about 16% from the bulk value, while the second-to-third spacing contracts by about 5%. These results agree closely with the latest evidence from LEIS.[10] In addition, we report a barely significant lateral relaxation in the second copper layer, and a buckling in the third Cu layer of about 0.07 Å. The possibilities of both these latter relaxations have been recognized in a very recent study of the corresponding surface of nickel.[26] Interestingly it appears that the half-monolayer coverage of O on the (110) surfaces of nickel and copper are very similar, even though the corresponding (100) surfaces are quite different.[16] Finally, for Cu(110)2×1-O, we find the two pairs of O–Cu bond lengths have values of 1.81 and 1.98 Å; the corresponding values from SEXAFS are 1.84 and 2.00 Å although different assumptions were made in that study.[6,7] The average O–Cu bond length found here is intermediate between the values in bulk Cu_2O (1.84 Å) and CuO (1.95 Å),[15] where O bonds to four neighboring Cu atoms in each case.

TABLE II. Ranges of parameter values (all in Å) (defined in Fig. 1) included in the more detailed analysis for the missing-row model of the Cu(110)2×1-O surface, and the optimal values which minimize R_{MZJ}.

	Range	Optimal
d_{01}	0.00 (0.02) 0.10	0.04
d_{12}	1.26 (0.05) 1.61	1.49
δ	−0.10 (0.05) 0.10	0.03
d_{23}	1.16 (0.05) 1.51	1.21
d_{33}	−0.10 (0.05) 0.10	0.07

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