

SURFACE STRUCTURE OF O/Cu(104) FACETS DETERMINED BY X-RAY DIFFRACTION

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We have determined the surface structure of O/Cu(104) using X-ray diffraction. This surface was prepared by dosing Cu(115) with oxygen, transforming the clean surface into facets with {104} and {113} orientations. This method of preparation, in essence, naturally grows the (104)-oriented substrate concurrent with the O-covered surface, resulting in O/Cu(104) facets which are smooth and highly ordered. Our results indicate that the top three atomic rows significantly expand away from the bulk, but no Cu rows are missing. The Cu–O structures of this surface are similar to those present on other O on Cu surface reconstructions, but the adsorbed O inhabits two adsorption sites with notably distinct geometries. The relationship between the O/Cu(104) and O/Cu(001)($2\sqrt{2} \times \sqrt{2}$) structures, in particular, is discussed.

1. Introduction

The traditional surface science method of preparing a surface is to cut a crystal as close as possible to the desired orientation. Limitations of this approach are that the resulting orientation is never perfect and will always admit a number of line and point defects (steps and kinks, respectively). It is usually hoped that most steps and kinks will be removed by annealing, leaving large areas of the desired surface. Under the appropriate conditions, a misoriented (and relatively high free energy) surface may facet into lower energy orientations as given by the Wulff construction.^{1–3} In certain cases this can be exploited to construct *perfect* surfaces from crystal surfaces with an altogether different orientation. In this paper we employ this method to prepare exact (104)-oriented surfaces via adsorbate-induced faceting^{4,5} from an approximately (115) starting orientation, taking advantage of the unusually low surface free energy of O/Cu(104).

One of the more studied examples of adsorption on single-crystal surfaces is that of oxygen on

copper. The reconstructions formed by O adsorption on low-index Cu are already well known, and are reviewed in Ref. 6. On Cu(110), O forms a (2×1) reconstruction⁷ at low coverage and a $c(6 \times 2)$ reconstruction at higher coverage.⁸ On Cu(001), the only stable O-induced reconstruction is $(2\sqrt{2} \times \sqrt{2})$ ⁹ (although other superstructures have been reported, and may be metastable). A common structural feature of these reconstructions¹⁰ is the formation of Cu–O–Cu chains on these surfaces. The O atoms are fourfold-coordinated, with all O–Cu bond lengths roughly 1.85 Å. These features are conspicuously similar to the characteristics of bulk cuprite, Cu₂O, except the O atoms of these reconstruction are not centered in Cu tetrahedra.¹⁰ O on Cu(111) induces a more complex series of reconstructions which are rotated relative to the substrate, yet are comparable with the structure of bulk Cu₂O(111) planes.^{11,12} Recent studies of O/Cu(102)(2×1) have also found evidence for Cu–O–Cu chains on this surface.^{13,14}

Unlike these low-index surfaces, most high-index Cu surfaces do not form stable reconstructions, but

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rather facet when exposed to oxygen. Specifically, the O/Cu(104) facet is formed after exposing a number of Cu(001) vicinal surfaces to O.^{15–24} Of course, to maintain the surface's macroscopic orientation, other facets must form across the surface as well, such as {001} for the faceting of Cu(106)²⁴ and Cu(108).²² For the particular case of Cu(115), previously observed by Sotto²¹ and by Reiter and Taglauer,^{23,25} the other facet is O/Cu(113). In this paper we use surface X-ray diffraction to describe the surface structure of the O/Cu(104) facets, resolving a long-standing controversy. We have discussed the structure of the O/Cu(113) surface and its (3×1) reconstruction elsewhere.^{26,27}

2. Previous Work on O/Cu(104)

Cu(104) is a (001) vicinal surface with $\langle 010 \rangle$ -type steps, i.e. $4(100) \times (010)$ in compact step notation.²⁸ The first four rows of atoms are all exposed to the surface (i.e. have reduced coordination); the steps are not close-packed, resulting in a surface which is not expected to be thermodynamically stable.²⁹ Our model of the O/Cu(104) surface, in Fig. 3, shows the surface unit cell and labels the atomic rows. We take z to be the surface normal, with x and y in the surface plane. x runs perpendicular to the steps of the surface (with the positive x direction pointing up the steps, i.e. to the right in Fig. 3); y is parallel to the surface steps.

Upon exposure to oxygen, however, this surface is known to become extremely stable.³⁰ The O/Cu(104) orientation is so strongly preferred that many nearby Cu(001) vicinal surfaces tend to form O/Cu(104) facets when exposed to O. Formation of O/Cu(104) facets has been observed by O dosing of many Cu surfaces, including Cu(115),^{21,23} Cu(117),²⁰ Cu(1, 1, 11),²⁰ Cu(1, 1, 16),¹⁹ Cu(102),¹⁸ Cu(106),²⁴ Cu(108)^{22,20} and Cu(418).¹⁹ As mentioned above, other facets must also form in order to maintain, on average, the macroscopic orientation of the surface.

Due to the $\langle 010 \rangle$ orientation of the steps of the (104) surface, the lateral separation of Cu step atoms (along a step) is 3.61 Å. This exposes gaps along the step edges which provide an ideal adsorption site for O, since 1.85 Å ($\approx 3.61 \text{ Å}/2$) is

the Cu–O bond length in Cu₂O and in several O-induced Cu reconstructions.¹⁰ In fact, the O–Cu–O linear chains which form along these steps are often considered the stabilizing building block of the O/Cu(001)($2\sqrt{2} \times \sqrt{2}$), O/Cu(110)(2×1) and O/Cu(110)c(6×2) reconstructions.¹⁰

Despite the importance of the (104) surface in the O on Cu system, a full structural determination has not been performed, and studies to date remain ambiguous. Algra *et al.*³¹ found, using low energy ion scattering, only one type of O adsorption site in Cu(104) for low O exposures, concluding that O₂ adsorbs dissociatively into the hollow sites of the steps. A photoelectron diffraction study by Thompson and Fadley³⁰ confirmed that O resides at the twofold step sites at low exposure, but at higher coverage also occupies a (001) terrace site, as proposed by Perdereau and Rhead.¹⁷ More recently, Robinson, Vlieg and Ferrer⁹ hypothesized that O would sit in the hollow sites of the first and third Cu rows, and that the fourth Cu row would be missing; the (001) terraces on the vicinal surface would then have a structure similar to the $(2\sqrt{2} \times \sqrt{2})$ reconstruction of O/Cu(001). In the $(2\sqrt{2} \times \sqrt{2})$ reconstruction, the O atoms are fourfold-coordinated; if O atoms sit at the center of the first- and third-row hollow sites of *unrelaxed* Cu(104), then the O atoms in the third row have five Cu neighbors *unless* the fourth Cu row is removed. Rutherford backscattering and channeling experiments^{21,32} were not able to directly observe O on the Cu(104) surface, but did find a large outward expansion of the top atomic layers of $\sim 0.3 \text{ Å}$. A missing row was not needed to interpret this data, yet the data were consistent with the third or fourth row missing.

Several STM studies have examined the structure of O/Cu(104) facets formed by exposing various Cu(001) vicinal surfaces to O. Lloyd and Woodruff²² initially labeled the O/Cu(104) facets of Cu(108) as missing the *second* Cu row, based on one STM image. Knight, Driver and Woodruff²⁴ reinterpreted that image as more likely missing the fourth row of Cu, consistent with their higher quality images of O/Cu(104) formed by faceting of Cu(106). Reiter and Taglauer²³ interpreted their images of O/Cu(104) from the faceting of Cu(115) as missing the fourth Cu row.

3. Present Experiment and Results

In order to conclusively determine the surface structure of O/Cu(104), we have performed surface X-ray diffraction on the (104) [and equivalent (014)] facets. Experiments were performed in the UHV chamber³³ at beamline X16A of the National Synchrotron Light Source, Brookhaven National Lab. The clean surface was prepared by chemical polishing, then by cycles of sputtering with 1 keV Ar⁺ ions and annealing to 550°C, until terraces on the surface were $\gtrsim 700$ Å, as determined by the widths of crystal truncation rods. The faceted surface was then formed by exposing the clean Cu(115) surface to ~ 50 L O₂ (1 L = 1 langmuir = 10^{-6} Torr sec) at 308°C. Faceting was observed with the X-rays²⁶ until (104), (014) and (113) facets had formed.

A crystal truncation rod (CTR), the primary diffraction feature of a surface, occurs because the surface breaks the periodicity of the bulk crystal.³⁴ Although typically thought of in terms of scattering from a macroscopic surface, CTRs will be produced by well-oriented facets as well. For the present case, three CTRs intersect each bulk peak, one for each facet orientation, as shown schematically in Fig. 1(a). We have observed the CTRs from these three facets with surface X-ray diffraction. Figure 1(b) is a cross-section through reciprocal space at constant perpendicular momentum transfer $\ell = \mathbf{q} \cdot \mathbf{c}$. The plane is thus parallel to the (115) surface with ℓ slightly less than that of the bulk Bragg peak. No longer is this surface (115)-oriented; if it were, a CTR would pass through the center of this plot at $h = 6, k = 0$ [in the units of the (115) surface]. Instead, the plot cuts through three rods, all of which are angled towards the bulk peak and perpendicular to the plane of their particular facet. The constant- ℓ plane cutting through the three CTRs is depicted by the h - k plane in Fig. 1(a). The well-defined orientations of the facets permit structure factors to be measured along the rods of each facet.

For this preparation, the coherence length in x (which we define as the direction perpendicular to the steps) on the (104) facets was approximately 400 Å, as judged by CTR halfwidths; in y , the coherence length was approximately 700 Å. All structure factor measurements were performed after O dosing had ended and the sample had been cooled to room temperature. The structure factors (F_{hkl}),

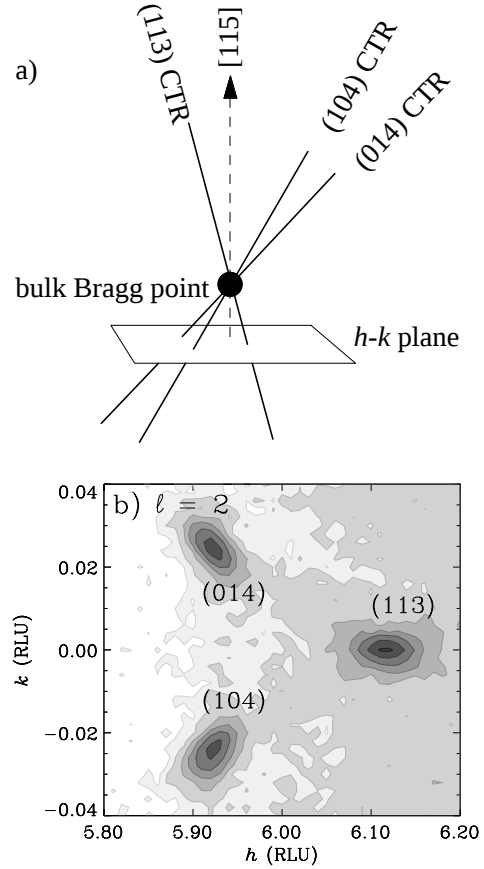


Fig. 1. (a) Schematic reciprocal-space diagram of facet CTRs. (b) A cross-section through reciprocal space below the $(603)_{115}$ bulk point, corresponding to the plane in (a). The three spots are located at the intersection of the $\ell = 2$ plane and the CTRs of the three facets formed by exposing O to Cu(115), as labeled. No (115) rod is visible at $h = 6, k = 0$, indicating that the surface is entirely faceted.

derived from integrated intensities of diffractometer ϕ scans, were corrected for Lorentz and polarization factors and the variation of the illuminated area on the surface.

As discussed above, the CTRs arising from these facets were no longer perpendicular to the Cu(115) surface, but instead each set of rods were perpendicular to the facet plane from which they arose. To index these rods, we switch to the notation of the particular facet. Operationally, this was very easy to achieve by appropriately relabeling all of the alignment reflections in the diffractometer's orientation matrix. The reciprocal space transformation from

standard fcc units to the (104) surface units is given by

$$\begin{pmatrix} h \\ k \\ \ell \end{pmatrix}_{(104)} = \begin{pmatrix} 4 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 4 \end{pmatrix} \begin{pmatrix} H \\ K \\ L \end{pmatrix}_{\text{fcc}}. \quad (1)$$

Thus, the fcc reflection $(111)_{\text{fcc}}$ is labeled, in the new surface coordinates, $(401)_{104}$ [and $(603)_{115}$, in Fig. 1(b)]. Bulk peaks for the (104) surface are separated in ℓ by 17 reciprocal lattice units, and are connected by CTRs perpendicular to the (104)

surface. In the tetragonal unit cell, $a = c = 14.90 \text{ \AA}$; $b = 3.615 \text{ \AA}$.

Along with structure factors from O/Cu(104), we measured the structure factors from the crystallographically equivalent O/Cu(014) facets, finding, as expected, that the data from both facets agreed well. Therefore, to achieve a better data set we averaged the measurements from the two facets together, along with the symmetry equivalents from each facet (using the pm symmetry of the surface, and the inversion symmetry $|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{\ell}}|$ of diffraction). In all, we measured 319 structure factors using 7.9 keV

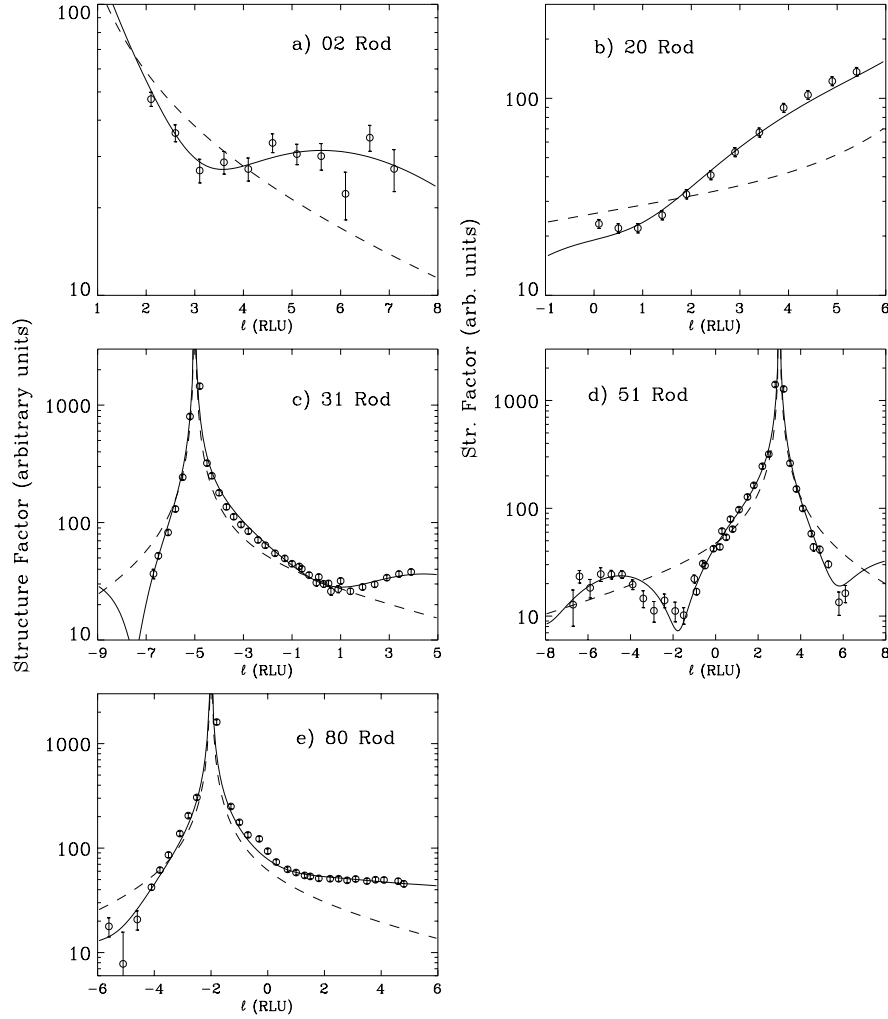


Fig. 2. Structure factors of the five CTRs of O/Cu(104) facets. Circles represent data points; the dashed line is a fit for an abrupt bulk termination, without atomic displacements or multiple Debye–Waller factors ($\chi^2 = 37.3$); and the solid line is the best fit as described in the text ($\chi^2 = 5.5$). (a) (02ℓ) rod, whose bulk peak is at $\ell = 0$; (b) (20ℓ) rod, whose bulk peak is at $\ell = 8$; (c) (31ℓ) rod, whose bulk peak is at $\ell = -5$; (d) (51ℓ) rod, whose bulk peak is at $\ell = 3$; (e) (80ℓ) rod, whose bulk peak is at $\ell = -2$.

Table 1. Refined parameters for the O/Cu(104) surface structure, resulting in $\chi^2 = 5.5$. Displacements are in fractions of the surface unit cell, whose dimensions are $a = c = 14.90 \text{ \AA}$; $b = 3.615 \text{ \AA}$. For Cu atoms, displacements are relative to bulk-inferred positions. Displacements for O atoms are relative to the Cu atoms of the same layer. Uncertainties for Cu atom displacements are $\sim 2 \times 10^{-3}$ for Δz_i , $\sim 1 \times 10^{-3}$ for Δx_i , and about twice that for O atoms.

Atom	Layer i	Δz_i	Δx_i	B (Debye–Waller factor)
O	1	+0.028	−0.003	~ 0
O	3	+0.015	+0.016	~ 0
Cu	1	+0.025	−0.0157	$1.8 \text{ \AA}^2$
Cu	2	+0.019	+0.0125	$1.8 \text{ \AA}^2$
Cu	3	+0.023	+0.0022	$1.8 \text{ \AA}^2$
Cu	4	−	+0.0046	$0.55 \text{ \AA}^2$
Cu	5	−	+0.0036	$0.55 \text{ \AA}^2$

X-rays, which symmetry-average to 127 data points (average agreement = 5.2%) along the five inequivalent rods shown in Fig. 2.

The structure factors along each truncation rod are strongly modulated, indicating a drastic modification of the surface structure away from a simple bulk truncation (represented as dashed lines in Fig. 2). Although the oscillations may be suggestive of a missing row, in fact no such structure simultaneously fits the oscillations on all five rods. Instead, our best fit to the data is a model with *all rows present*, and O atoms in the hollow sites of the first row (step edge) and third row (terrace). The displacements of the atoms in the first five rows are listed in Table 1, with calculated structure factors displayed as solid lines in Fig. 2. Allowing further atomic displacements did not improve the fit. Excluding the O atoms from the model, while refining the same number of Cu displacements, results in a χ^2 value more than double that of our best model.

In our model of the surface, the first three rows of atoms relax upwards, away from the bulk. The average spacing between atoms in the top three rows and atoms in lower layers increases by $\sim 9\%$, fully consistent with ion channeling studies.³² With the first three rows expanding away from the bulk, the comparison with the O/Cu(001)($2\sqrt{2} \times \sqrt{2}$) superstructure^{9,23} remains partially valid, even without the fourth row absent. Apparently, the expansion of the first three rows carries a lower energy cost than removing the fourth row. Views of the relaxed structure are shown in Fig. 3.

One notable result of this analysis is that the facets are, within error, completely smooth: $\sqrt{\sigma^2} = 0 \pm 0.1 \text{ \AA}$, as might be expected from the stability of the O/Cu(104) facets. That is, on the length scale of the facets, the steps on the surface are straight (unkinked) and unbunched, in agreement with the micrographs of Reiter and Taglauer.²³ While defects such as dislocations and impurities on the clean surface might be sites where facets nucleate, they will not occur on the facets themselves, resulting in very smooth facet surfaces.

Besides a Debye–Waller factor for the bulk Cu atoms of $B_{\text{bulk}} = 0.55 \text{ \AA}^2$, the Cu atoms of the first three rows had a separate factor, $B_{\text{surface}} = 1.8 \pm 0.2 \text{ \AA}^2$. The refined Debye–Waller factor of the O atoms was zero, within error bars. In all, four displacement parameters were used for O atoms and eight for Cu atoms. Due to the fewer electrons in O than in Cu and the correspondingly smaller form factor, the positions of the O atoms are determined with slightly lower certainty than the Cu positions. Despite this model’s excellent ability to reproduce the modulations of the structure factor along all five rods, the goodness-of-fit parameter is relatively large: $\chi^2 = 5.5$. This is attributable to small imperfections of the fitting [most of which is around (513); Fig. 2(d)] coupled with the very small error bars from the highly reproducible data. The χ^2 test weights each data point with the inverse square of the error, yielding a high goodness-of-fit measure even for good fits to data with very small uncertainties.

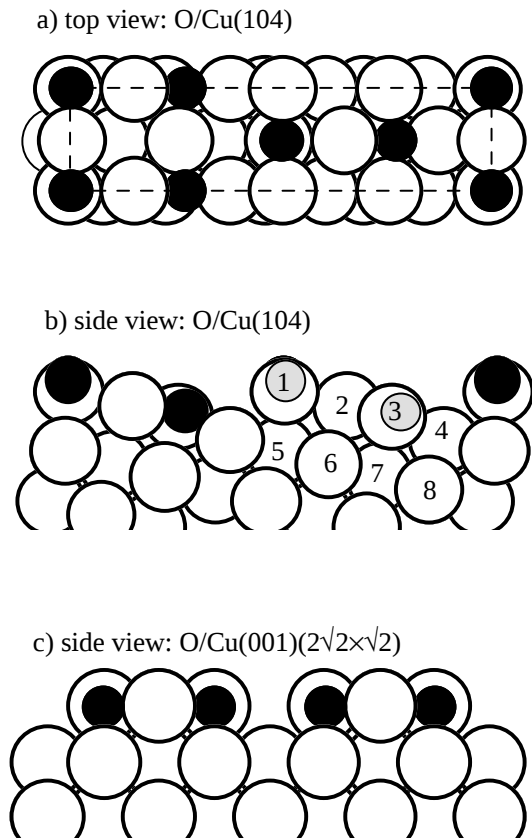


Fig. 3. (a) Plan and (b) side views of refined O/Cu(104) surface structure. Cu atoms are hollow; O atoms are filled. Gray atoms in (b) are O atoms hidden by Cu. The surface unit cell is outlined in (a), and the rows are numbered in (b). (c) Side view of (unrelaxed) O/Cu(001)($2\sqrt{2} \times \sqrt{2}$) structure, for comparison.

4. Discussion

The O/Cu(104) surface is in some aspects similar to that of O/Cu(001)($2\sqrt{2} \times \sqrt{2}$), even though the vicinal surface structure [Fig. 3(b)] is not as close to that of the low-index surface [Fig. 3(c)] as originally thought. In O/Cu(001)($2\sqrt{2} \times \sqrt{2}$), the O atoms would be overcoordinated if every third Cu row were not absent. While no Cu rows are missing from O/Cu(104), the top three rows are expanded vertically, reducing the O coordination.

The one striking dissimilarity between the O/Cu(104) and O/Cu(001)($2\sqrt{2} \times \sqrt{2}$) structures is that the two O sites of O/Cu(104) (in the first and third rows) are inequivalent. The O in the third row (terrace site) is fourfold-coordinated with bonds ~ 1.84 Å to the Cu atoms in the second, third and fourth rows; this is almost a planar structure quite

unlike the O coordination on the ($2\sqrt{2} \times \sqrt{2}$) structure or in bulk Cu₂O. The Cu–O–Cu bond angles for this O (row 3) are 160° parallel to the step edge (both Cu atoms in row 3) and 152° perpendicular to the step (Cu atoms in rows 2 and 4). The O in the first row (step-edge site) is only twofold-coordinated; it is located 1.85 Å from the adjoining Cu step atoms, but then >2.4 Å from the next nearest Cu atoms. Cu–O–Cu chains, without the fourfold coordination of O, are thus the main feature at this O site. The Cu–O–Cu bond angle along this chain (parallel to the step) is 154° . Table 2 details the nearest-neighbor Cu–O bond lengths resulting from our fit. The marked asymmetry in binding sites is not too surprising; on this stepped, vicinal surface, the O adsorption sites should not be degenerate as are the sites on the symmetrical ($2\sqrt{2} \times \sqrt{2}$) surface. The steps on this vicinal surface produce the asymmetry in O adsorption sites observed in this work and previous studies.^{31,30} We expect that this asymmetry, not present on ideal (nonmiscut) O/Cu(001)($2\sqrt{2} \times \sqrt{2}$), significantly affects any rehybridization of Cu–O bonds.³⁵ This should be apparent in valence-band spectroscopy and in any future theoretical calculations which compare the total energies of the various O/Cu(104) surface structure models.

We expect that our results for the O/Cu(104) facets should fully describe the structure of bulk O/Cu(104) single crystal surfaces. As discussed in Ref. 26 and elsewhere, O/Cu(104) is one of the most stable O-covered Cu surfaces, and the formation of O/Cu(104) facets appears to drive the faceting of this system. It is conceivable that these facets may, in fact, be closer to the lowest-energy structure of O on Cu(104) than even O/Cu(104) from bulk single crystals. Bulk crystals may be hampered by misorientation, impurities or incomplete O adsorption, while the facets are less susceptible to such limitations. In our preparation we are, in effect, growing the {104} substrate along with its surface, which results in a high quality substrate of reasonable (but necessarily limited) lateral scale. It is even conceivable that the (115) starting orientation may produce better facets than one closer to (104), since that starting surface has no bias to (104) vs. (014), and the residual (113) facet is easily accessible. Use of such a growth method is compatible with any surface science technique with sufficient spatial or orientational resolution, in order to resolve the signal from the

Table 2. O–Cu nearest neighbor distances for the two O adsorption sites on Cu(104), with uncertainties ~ 0.04 Å, based on refined atomic coordinates (Table 1). In contrast, for unrelaxed Cu atoms and O atoms centered in their adsorption site, then $d_{\text{O–Cu}} = 1.807$ Å for each interatomic distance in the table.

O atom site	Cu location	$d_{\text{O–Cu}}$ (Å)	Coordination
step (row 1)	row 1	1.855	2
	row 2	2.410	1
	row 5	2.540	1
terrace (row 3)	row 2	1.847	1
	row 3	1.837	2
	row 4	1.842	1
	row 6	2.420	1

desired facets [O/Cu(104) in this case] with that from other orientations [O/Cu(113) here].

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